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Extended Wagner-type models and their application to the prediction of the transition from internal to external oxidation

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Abstract

Recent works have paved the way to theoretical predictions of the conditions governing the transition from internal to external oxidation of metals and alloys: such conditions directly result from Wagner (1959)'s classical analytical model, provided that it is made to incorporate a heuristic decrease of diffusion coefficients upon the fraction of oxides, aimed at representing their "barrier effect" upon diffusion. The aim of this paper is to extend these works by removing some of the very restrictive hypotheses introduced by Wagner (1959). First, the formulation initially limited to small fractions of oxides is extended to arbitrarily large fractions. Even in their modified form, the equations are still solvable entirely analytically, albeit with a change of the predicted value of the "critical" fraction of oxides, above which internal oxidation must give way to external oxidation. The new value is in better agreement than previous ones with the scarce available experimental estimates. Second, the formulation is extended to finite - instead of infinitesimal - values of the solubility product governing local chemical equilibrium between the oxide and the chemical elements dissolved in the metallic matrix. The nonlinear equations of the diffusion/precipitation problem then become much more complex and amenable only to some hybrid analytical/numerical solution. The results, although interesting, raise a number of issues essentially tied to the basic hypothesis made of *instantaneous local thermodynamic equilibrium.* It is finally shown, using a simplistic, prototype kinetic model of oxide precipitation, that relaxation of this hypothesis should permit to solve at least some of these issues.

Keywords: Internal/external oxidation; Wagner's model; oxides as diffusion barriers; large oxide fractions; instantaneous local thermodynamic equilibrium; kinetic models of precipitation

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1 Introduction

Sixty-three years after its publication, Wagner (1959)'s theoretical analysis of internal oxidation of metals and alloys remains a cornerstone of this branch of metallurgy. Wagner (1959)'s analytical solution pertains to the archetypal 1D problem, schematized in Figure 1, of isothermal internal oxidation of a semi-infinite homogeneous steel sheet, occupying the domain $0 \leq x < +\infty$, initially containing no oxygen (O) but a given nonzero concentration of a single oxidizable element (A), determined by the grade of the steel. Two diffusion processes occur simultaneously: (i) O diffuses inwards from the surface of the sheet (at $x = 0$), where its concentration $C_O = C_O^{\text{surf}}$ is prescribed - typically because of contact with some external atmosphere containing water molecules dissociating on the surface; and (ii) outward diffusion of A from the deep regions of the sheet (at $x \to +\infty$) where its concentration $C_A = C_A^{\text{core}}$ is prescribed - *via* the composition of the steel. The diffusion of O is accelerated, and that A is generated, by "pumping" of O and A atoms due to some chemical reaction occurring in some intermediate region, and leading to formation of some "precipitated" oxide of formula OA_ν.

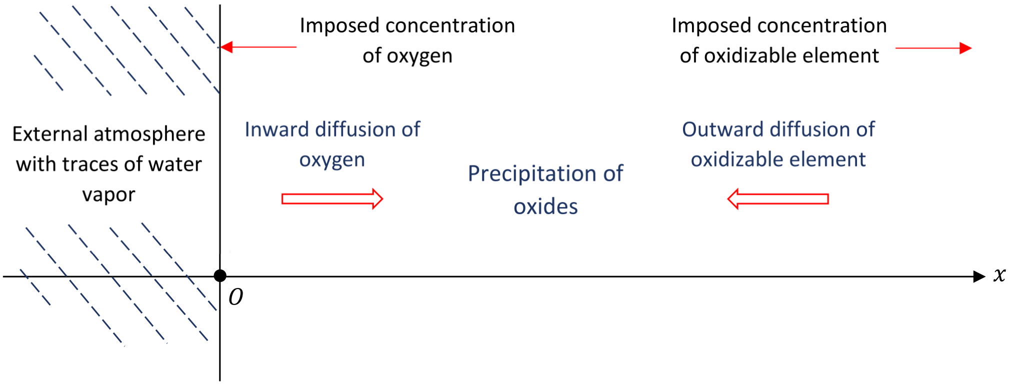

Fig. 1. Wagner (1959)'s archetypal internal oxidation problem.

In Wagner (1959)'s version of the problem, local thermodynamic equilibrium between the phases is assumed to prevail at every position and instant; the law of mass action expressing this equilibrium states that $C_O C_A^\nu = K$ where K denotes the solubility product of the oxide OA_ν. In addition K is assumed to be so exceedingly small - that is, element A so highly oxidizable - that O and A cannot coexist in their dissolved form in the metallic matrix: thus either C_O or C_A must be zero at every point and at each instant. As a consequence, the region where the chemical reaction takes place at a given instant reduces to some infinitely thin *oxidation front* located somewhere in the sheet, say at $x = \xi(t)$. (The determination of $\xi(t)$ is of course an integral part of the solution of the problem). Thus, before the front has swept a given point x ($\xi(t) < x < +\infty$), C_O is zero there so that the reaction cannot start; and after the passage of the front at the point x ($0 \leq x < \xi(t)$), C_A is in turn zero there so that the reaction necessarily stops. Furthermore, it will be shown below that as a consequence of the infinite thinness of the zone where oxidation takes place at any instant, the fraction P of oxides is uniform within the oxidized zone $0 \leq x < \xi(t)$. All of these features are illustrated in Figure 2, which provides a qualitative representation of the spatial distributions of C_O, C_A and P at a given instant.

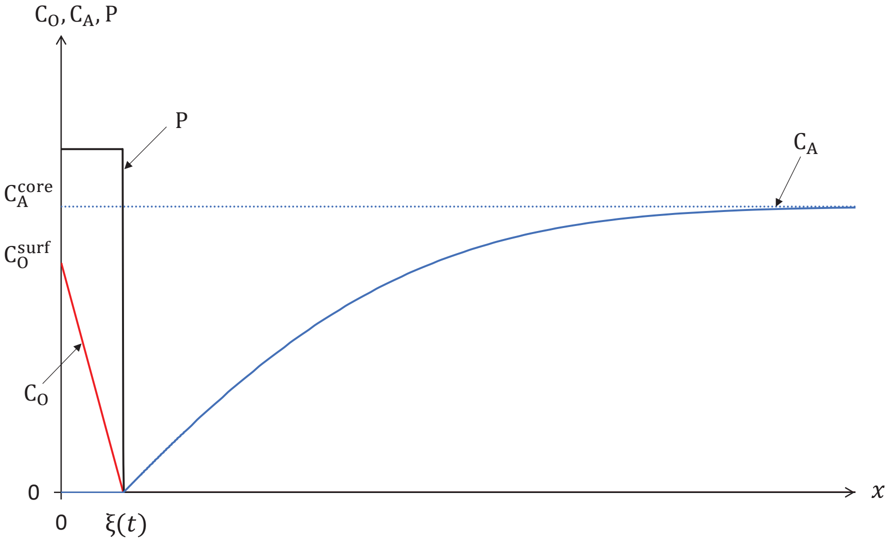

Fig. 2. Qualitative features of Wagner (1959)'s solution (for an infinitesimal solubility product).

The impact of Wagner (1959)'s model and solution may be appreciated from the numerous works they inspired. Critical discussions of the original theory and some of its improved later variants were offered by Rapp (1965) and Douglass (1995). Many efforts were also devoted to the relaxation of Wagner's various restrictive assumptions - limitation to a single oxidant and a single oxidizable element, forming a single oxide with an extremely low solubility product, etc.: see the works of (Kirkaldy, 1969; Laflamme and Morral, 1978; Ohriner and Morral, 1979; Whittle *et al.*, 1981; Christ *et al.*, 1986; Stott and Wood, 1988; Fortunier *et al.*, 1995; Gesmundo and Gleeson, 1995; Huin *et al.*, 1996; Gesmundo *et al.*, 1996, 1997, 1998; Gesmundo and Niu, 1999; Niu and Gesmundo, 2001; Huin *et al.*, 2005; Leblond, 2005; Brunac *et al.*, 2010; Leblond *et al.*, 2017), among others. These various efforts greatly widened the domain of application and significance of Wagner (1959)'s original work.

The relation between Wagner (1959)'s analysis and the prediction of conditions governing the transition from *internal oxidation* - wherein oxides are formed in the interior of the sheet - to *external oxidation* - wherein precipitation of oxides remains confined to the surface - was noted by Wagner himself. Such conditions may indeed be obtained by combining his expression of the fraction P of oxides in the oxidized zone, with some postulated value of the "critical" fraction P^{crit} above which the transition is expected to occur. However, in spite of the continued attention paid to Wagner (1959)'s work, it was not until a few years ago that the remark was made by Leblond (2011) that there was no need to *postulate* such a value of P^{crit}, because it could be deduced *from the equations of the model itself*, in a suitably extended and modified form. Leblond (2011)'s suggested overhaul of the governing equations of the oxidation problem consisted of heuristically assuming - following a much earlier suggestion of Kirkaldy (1969) - the diffusion coefficients of elements to be decreasing functions of the local fraction of oxides, so as to account for the "barrier effect" of these oxides upon diffusion.

Leblond (2011)'s mathematical presentation was reformulated by Zhao *et al.* (2015) in a more physical format. An intuitive understanding of the mechanism evidenced by Leblond (2011) may be gained through the following considerations:

- One typical, and somewhat paradoxical, feature of the analytical solution of Wagner (1959)'s original equations is that a *decrease* of the ratio $\phi \equiv D_O/D_A$ of the diffusion coefficients D_O of oxygen and D_A of the oxidizable element A, induces an *increase* of the fraction P of oxides in the oxidized zone. In qualitative terms, this is because if O diffuses more slowly, this leaves more time for A to diffuse from the interior of the plate toward its surface, so as accumulate and be oxidized there.
- Now solve Wagner (1959)'s equations, in a first step, without accounting for the influence of P upon D_O and D_A; the solution yields a first estimate $P^{(1)}$ of the oxide fraction in the oxidized zone.
- In a second step, account for the influence of P upon D_O and D_A using $P^{(1)}$ as an estimate. Since O is present only in the oxidized zone and A only in the non-oxidized zone, this induces a decrease of D_O but no change of D_A, and therefore a decrease of the ratio ϕ. Solve Wagner (1959)'s equations again; the second estimate $P^{(2)}$ of P obtained thus is *larger than* $P^{(1)}$, as a result of the decrease of ϕ.
- Account for the influence of P upon D_O and D_A using the estimate $P^{(2)}$ instead of $P^{(1)}$, solve the equations again, and repeat the process *ad infinitum*. The increasing sequence of successive estimates $P^{(1)}, P^{(2)}...$ of P obtained in this way may either converge or diverge, depending on the parameters of the problem. Convergence means that a solution to the nonlinear equations of internal oxidation is obtained; but divergence means that *such a solution does not exist*, so that *external oxidation* (implying an infinite concentration of oxides on the surface of the plate) *must take over*.

In Leblond (2011)'s work the effect of diffusion barriers was modelled, following Kirkaldy (1969)'s elementary suggestion, by reducing diffusion coefficients proportionally to the volume fraction of oxides. This simplistic hypothesis was later refined by Leblond *et al.* (2013) using finite element simulations aimed at precisely quantifying the effect of obstacles of various shapes upon diffusion. This resulted in a decrease of the estimated critical fraction P^{crit} of oxides, bringing it to somewhat closer agreement with Rapp (1961)'s experimental estimate for the O/In/In_2O_3 system in an Ag matrix.[1]

Leblond (2011)'s analysis, even in its refined version (Leblond *et al.*, 2013), suffered from inevitable drawbacks tied to the severely restrictive hypotheses originally introduced by Wagner (1959), some of which were recalled above. It is the aim of this paper to try and remove at least two of these restrictions. The first is that Wagner (1959)'s model is basically limited to *small concentrations of elements and fractions of oxides*, whereas Leblond (2011)'s and Leblond *et al.* (2013)'s estimates of the critical oxide fraction P^{crit} derived from the model are comparable to unity; which raises an issue of internal consistency of the model. The second severe restriction of Wagner (1959)'s analysis relates to limitation to oxides having an *extremely low solubility product*, implying concentration of the zone where oxidation actually occurs at a given instant within some precipitation front of measure zero. Such a hypothesis is reasonable for some systems, like O/Al/Al_2O_3 in a

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[1] There are many experimental estimates in the metallurgical literature of the critical *core fraction of oxidizable element* governing the transition, but Rapp (1961)'s work seems the only one that provides an estimate of the critical *fraction of oxides*.

Fe matrix, but not for many others, like for instance O/Mn/MnO in a Fe matrix; for the latter type of system the active oxidation zone is spread over some interval of nonzero, finite length.

The paper is organized as follows:

- Section 2 presents a general model of coupled diffusion of chemical elements and formation of "precipitate" phases within solid matrices, accounting for possible large fractions of these phases. This model is similar to that proposed by Brunac *et al.* (2010), but for somewhat modified right-hand sides of the diffusion equations.
- Section 3 extends, in the case of an infinitesimally small solubility product, Wagner (1959)'s and Leblond (2011); Leblond *et al.* (2013)'s solution to the improved model of Section 2 accounting for large fractions of precipitates. The solution is still accessible by purely analytical means; it leads to a new and smaller value of the critical fraction of oxides governing the transition from internal to external oxidation.
- Section 4 considers the more complex case of a nonzero, finite solubility product of the oxide. The problem is then no longer amenable to some fully analytical solution. The method of solution proposed, inspired from that of Huin *et al.* (2005) for a simpler version of the problem, consists of a "mixed" analytical/numerical approach. The results obtained, though promising, raise some issues pertaining to phenomena occurring near the surface of the plate; these issues are intimately connected to the basic hypothesis of *instantaneous local thermodynamic equilibrium* between the phases, made in all works on the topic up to now.
- In Section 5, it is finally shown qualitatively that the replacement of this hypothesis through some kinetic law of precipitation of oxides should solve at least some of the issues evidenced in Section 4. The prototype kinetic equation used for this purpose does not make any claim on physical realism and is used for purely pedagogical reasons; the development of coupled equations of diffusion and precipitation involving a realistic model of nucleation and growth of oxides is left for future work.

2 Extended model of coupled diffusion/precipitation accounting for large fractions of precipitates

This Section is essentially based on the work of Brunac *et al.* (2010). However the right-hand sides of the diffusion equations will differ somewhat from those in the previous work, for reasons that will be explained.

2.1 General hypotheses and notations

The material considered consists of a matrix phase (in practice generally Fe) denoted M, which contains mobile, dissolved chemical elements plus a number of immobile, "precipitate" phases collectively denoted P. The representative volume elements (RVEs) considered, a prototype of which is schematized in Figure 3, are sufficiently large to each contain the M phase plus all types of P phases, but nevertheless small enough for local variations of chemical composition to be negligible within each of them.

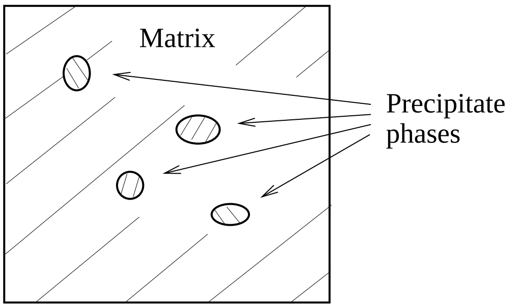

Fig. 3. Schematic RVE considered by the model.

The M phase contains N_e distinct types of chemical elements denoted with a Latin index $i = 1, ..., N_e$. The atomic mass, total mass fraction (in the M and P phases) and mass concentration (in the M phase) of element i are denoted m_i, F_i and C_i respectively. The total mass fractions F_i are defined in reference to the *total mass of the RVE* (M+P phases) - this is natural since the atoms of each chemical species are potentially present in all types of phases. On the other hand the mass concentrations C_i are defined in reference to the *mass of the sole M phase* contained within the RVE - as they must in order to possess a thermodynamic significance warranting their appearance in the laws of mass action, see Subsection 2.4 below. The C_i's are assumed to be much smaller than unity (*hypothesis of dilute solution*), but the F_i's are not, because the fractions of the P phases may be large; see below.

Within the M phase are embedded N_p distinct P phases, denoted with a Greek index $\alpha = 1, ..., N_p$. The molar mass, solubility product and mass fraction - defined in reference to the total mass of the RVE - of phase α are denoted M_α, K_α and P_α, respectively. The P_α's may be comparable to unity (possibly *large fractions of precipitate phases*). The stoechiometric coefficient of element i in phase α (number of atoms of this element per molecule of this phase) is denoted $N_{\alpha i}$.[2]

2.2 Balance equations

When establishing the balance equations, one must beware of the different reference masses used in the definitions of the total mass fractions F_i of the elements and their mass concentrations C_i in the matrix. Consider a volume of material of unit mass of material containing all phases:

- The total mass of element i in this volume is F_i so that the total number of moles of this element is F_i/m_i.

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[2] In the work of Leblond *et al.* (2017), more complex *non-stoechiometric* precipitate phases with variable chemical composition were envisaged. The analyses expounded in the present work do not require considering such complexities.

- The cumulated mass of all P phases is $\sum_{\alpha=1}^{N_p} P_\alpha$ so that the mass of the M phase is $1-\sum_{\alpha=1}^{N_p} P_\alpha$; within the latter phase, the mass concentration of element i is C_i so that the mass of this element is $\left(1-\sum_{\alpha=1}^{N_p} P_\alpha\right) C_i$, and the corresponding number of moles is $\left(1-\sum_{\alpha=1}^{N_p} P_\alpha\right) C_i/m_i$.
- The mass of phase α is P_α, so that there are P_α/M_α moles of this phase, containing $N_{\alpha i} P_\alpha/M_\alpha$ moles of element i.

It follows from these elements that the balance equation of element i reads

$$\frac{F_i}{m_i} = \left(1-\sum_{\alpha=1}^{N_p} P_\alpha\right)\frac{C_i}{m_i} + \sum_{\alpha=1}^{N_p} N_{\alpha i}\frac{P_\alpha}{M_\alpha} \qquad (i = 1,\ ...,\ N_e). \tag{1}$$

2.3 Diffusion equations

The flux-vector of element i is classically assumed to be of the form $-\overline{D}_i\,\mathbf{grad}\,C_i$, where $\overline{D}_i$ is some coefficient.[3] Expressing the rate of the total mass fraction of element i within the RVE as minus the integral of this flux over its boundary and using the divergence theorem, one gets the diffusion equation of this element in the form

$$\frac{\partial F_i}{\partial t} = \mathrm{div}\left(\overline{D}_i\,\mathbf{grad}\,C_i\right) \qquad (i = 1,\ ...,\ N_e). \tag{2}$$

It remains to relate the coefficients $\overline{D}_i$ to the standard diffusion coefficients D_i of elements. In order to do so, consider the special case where the fractions P_α of all P phases are constant in time and space (*inactive* and *uniform* precipitation). Then by equation (1), $\partial F_i/\partial t = \left(1-\sum_{\alpha=1}^{N_p} P_\alpha\right)\partial C_i/\partial t$ so that equation (2) takes the form

$$\frac{\partial C_i}{\partial t} = \frac{1}{1-\sum_{\alpha=1}^{N_p} P_\alpha}\,\mathrm{div}\left(\overline{D}_i\,\mathbf{grad}\,C_i\right) = \mathrm{div}\left(\frac{\overline{D}_i}{1-\sum_{\alpha=1}^{N_p} P_\alpha}\,\mathbf{grad}\,C_i\right) \quad (i = 1,\ ...,\ N_e).$$

Comparison with the equation defining the standard diffusion coefficient D_i, $\partial C_i/\partial t = \mathrm{div}\,(D_i\,\mathbf{grad}\,C_i)$, yields

$$\overline{D}_i = \left(1-\sum_{\alpha=1}^{N_p} P_\alpha\right) D_i \qquad (i = 1,\ ...,\ N_e). \tag{3}$$

It is worth noting here that in Brunac *et al.* (2010)'s work, the reasoning just expounded was absent and as a consequence the coefficients $\overline{D}_i$ were merely, and wrongly, identified to the D_i's.

The standard diffusion coefficients D_i may themselves depend upon the fractions of precipitates, since the P phases may act as barriers to diffusion; this effect may be schematized

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[3] In a more general formulation, the flux-vector of a given element is considered to be proportional to the gradient of its *activity*, that is the product of its concentration and *Henry's coefficient*. Again, such complexities need not be envisaged here.

through a formula for the D_i's of the type

$$D_i = f(\mathbf{P}) D_i^0 \qquad (i = 1, ..., N_e) \tag{4}$$

where the D_i^0's are the diffusion coefficients in the absence of P phases, and $f(\mathbf{P})$ a function of the vector $\mathbf{P} \equiv (P_\alpha)_{\alpha=1,\ldots,N_p}$ of their fractions. Several formulae have been proposed for this function. An old but appealing suggestion of Kirkaldy (1969) consists of simply shrinking diffusion coefficients through multiplication by the volume fraction of the M phase; this leads, upon a simple calculation, to the following formula (Brunac *et al.*, 2010):

$$f(\mathbf{P}) = \frac{1 - \sum_{\alpha=1}^{N_p} P_\alpha}{1 + \sum_{\alpha=1}^{N_p} (v_\alpha / v_M \ - 1)\, P_\alpha} \tag{5}$$

where v_M and the v_α's denote the specific volumes (volumes per unit mass, inverses of the specific masses) of the M and various P phases, respectively. But homogenization theories show that expression (5) only represents an upper estimate of the function $f(\mathbf{P})$. Leblond *et al.* (2013) proposed the following more accurate formula, on the basis of finite element simulations of diffusion in a RVE in the presence of impenetrable obstacles having the shape of oblate spheroids with axis parallel to the direction of diffusion (schematically representing precipitates located in the sub-surface of an oxidized plate):

$$f(P) = \left[\frac{1 - P}{1 + (v_P / v_M - 1)\, P} \right]^{1 + 0.55\, W} . \tag{6}$$

In this formula P denotes the mass fraction of the (unique) P phase defined by the obstacles, v_P its specific volume, and W the shape factor of the obstacles, that is the ratio of their major to minor axes. (Note that the term [...] represents the volume fraction of the M phase like in equation (5)).

Combination of equations (2), (3) and (4) yields the final form of the diffusion equations:

$$\frac{\partial F_i}{\partial t} = \mathrm{div} \left[\left(1 - \sum_{\alpha=1}^{N_p} P_\alpha \right) f(\mathbf{P}) D_i^0 \, \mathbf{grad}\, C_i \right] \qquad (i = 1, ..., N_e) \tag{7}$$

with $f(\mathbf{P})$ given by equation (5) or (6). These equations differ from those of Brunac *et al.* (2010) through the factor $\left(1 - \sum_{\alpha=1}^{N_p} P_\alpha\right)$ in the right-hand side, which was overlooked by these authors for the reason explained above. Note that this factor does *not* arise from the role of barriers to diffusion played by the P phases, but simply from the different reference masses used in the definitions of the variables F_i and C_i appearing in the left- and right-hand sides, respectively.

2.4 Laws of mass action

Precipitation of P phases is described in a global way through the laws of mass action, which express the hypothesis of instantaneous local thermodynamic equilibrium between the M and various P phases:

$$\begin{cases} P_\alpha = 0 \ \text{ and } \ \displaystyle\prod_{i=1}^{N_e} C_i^{N_{i\alpha}} \le K_\alpha \\ \text{or} \\ P_\alpha > 0 \ \text{ and } \ \displaystyle\prod_{i=1}^{N_e} C_i^{N_{\alpha i}} = K_\alpha \end{cases} \qquad (\alpha = 1, 2, ..., N_p). \tag{8}$$

Note that the mass fractions C_i here *must* be defined by dividing the mass of atoms of element i in the M phase by the mass of this sole phase (*not* by the total mass of all phases), in order to represent the concentrations of elements within the matrix.

2.5 Boundary conditions

For each element i, there are two possible basic boundary conditions :

$$\begin{cases} C_i \qquad\qquad = C_i^{\text{imp}} \\ \text{or} \\ \mathbf{grad}\, C_i \,.\, \mathbf{n} = 0 \end{cases} \qquad \text{on } \partial\Omega \tag{9}$$

where C_i^{imp} denotes some imposed value of C_i (enforced for instance through contact with an external atmosphere containing element i), and $\mathbf{n}$ the unit normal vector to the boundary $\partial\Omega$ of the domain considered. For each element, boundary conditions may also be of mixed type, that is equation $(9)_1$ on some part of $\partial\Omega$ and $(9)_2$ on the complementary part.

3 Analytical solution of the internal oxidation problem for an oxide with an infinitesimally small solubility product

The mathematical treatment in this Section is analogous to that in the works of Leblond (2011) and Leblond *et al.* (2013) (derived itself from that in the work of Wagner (1959)), but with somewhat more complex governing equations, owing to the incorporation into the model of possibly large fractions of P phases.

3.1 Generalities

We consider Wagner (1959)'s problem sketched in the Introduction, but with more general hypotheses detailed below. All quantities of interest are looked for in the form of functions of the sole variable $u \equiv x/\sqrt{t}$. With such a form, an important consequence of the reduction of the zone where oxidation occurs at a given instant to an infinitely thin front is that *the mass fraction P of oxides in the oxidized zone* $0 \leq x < \xi(t)$ *is a constant independent of* x *and* t. Indeed at a given time t and some given point x within the oxidized zone at this time, $0 \leq x < \xi(t)$, oxidation no longer occurs since the point has already been swept by the front; hence P no longer evolves, $\partial P/\partial t = 0$, so that $dP/du = 0$, and it follows that $\partial P/\partial x = 0$ also. This is *the* basic feature - illustrated in Figure 2 above - that permits to develop an analytic solution of the problem in spite of its non-linearity.

3.2 Equations of the problem

In the case considered, the general mass balance equations (1) take the following specific form:

$$\begin{cases} F_O = (1-P)C_O + \frac{m_O}{M_P}P & \text{for } 0 \leq x < \xi(t) \\ F_A = C_A & \text{for } \xi(t) < x < +\infty \end{cases} \tag{10}$$

where F_O and F_A denote the total mass fractions of elements O and A, and m_O and M_P the molar masses of O and the oxide OA_ν, respectively. Account has been taken in these equations of the fact that the value of the fraction of precipitated oxides is P in the oxidized zone $0 \leq x < \xi(t)$, and 0 in the non-oxidized zone $\xi(t) < x < +\infty$.

The general diffusion equations (7) take the following form for element O:

$$\frac{\partial F_O}{\partial t} = (1-P)\frac{\partial C_O}{\partial t} = \frac{\partial}{\partial x}\left[(1-P)f(P)D_O^0\frac{\partial C_O}{\partial x}\right] = (1-P)f(P)D_O^0\frac{\partial^2 C_O}{\partial x^2} \text{ for } 0 \leq x < \xi(t)$$

where D_O^0 denotes the diffusion coefficient of O in the absence of oxides acting as obstacles; use has been made here of the fact that P depends neither on x nor on t. This equation simplifies into

$$\frac{\partial C_O}{\partial t} = f(P)D_O^0\frac{\partial^2 C_O}{\partial x^2} \quad \text{for } 0 \leq x < \xi(t). \tag{11}$$

On the other hand the general diffusion equations (7) reduce for element A to

$$\frac{\partial C_A}{\partial t} = D_A^0\frac{\partial^2 C_A}{\partial x^2} \quad \text{for } \xi(t) < x < +\infty \tag{12}$$

where D_A^0 denotes the diffusion coefficient of A unperturbed by oxides (absent from the region $\xi(t) < x < +\infty$).

The diffusion equations (11, 12) are supplemented with the following initial and boundary conditions:

$$\begin{cases} C_O = 0 & \text{for } 0 < x < +\infty,\, t = 0 \\ C_A = C_A^{\text{core}} & \text{for } 0 < x < +\infty,\, t = 0 \end{cases} ; \quad \begin{cases} C_O = C_O^{\text{surf}} & \text{for } x = 0,\, 0 \leq t < +\infty \\ C_A = C_A^{\text{core}} & \text{for } x \to +\infty,\, 0 \leq t < +\infty. \end{cases} \tag{13}$$

These equations do not permit to determine the position $\xi(t)$ of the oxidation front. The key to doing this is to write an equality of fluxes at the position $x = \xi(t)$. At $x = \xi(t)^-$, there is a mass flux of O, oriented toward the right, equal to $-(1-P)f(P)D_O^0\,\partial C_O/\partial x$ in absolute value, corresponding to a molar flux of $-(1-P)f(P)(D_O^0/m_O)(\partial C_O/\partial x)$. At $x = \xi(t)^+$, there is a mass flux of A, oriented toward the left, equal to $D_A^0\,\partial C_A/\partial x$ in absolute value, corresponding to a molar flux of $(D_A^0/m_A)(\partial C_A/\partial x)$ where m_A denotes the molar mass of A. Since both of these fluxes serve to form molecules of chemical formula OA_ν, the molar flux of A must be ν times that of O; that is, the condition

$$\frac{D_A^0}{m_A}\frac{\partial C_A}{\partial x}\left[\xi(t)^+,t\right] = -\nu(1-P)f(P)\frac{D_O^0}{m_O}\frac{\partial C_O}{\partial x}\left[\xi(t)^-,t\right] \quad \text{for } 0<t<+\infty \tag{14}$$

must hold.

It finally remains to explain how to calculate the mass fraction P of oxides in the oxidized zone $0 \le x < \xi(t)$. This is most easily done through some intuitive reasoning.[4] Consider a small time-interval $[t, t+\delta t]$ during which the oxidation front moves toward the right by the amount $\delta\xi = \dot{\xi}(t)\,\delta t$. The input mass flux of A (per unit time) into the zone $[\xi(t), \xi(t)+\delta\xi]$ is $D_A^0\partial C_A/\partial x$. Integrated over the time-interval $[t, t+\delta t]$, this flux becomes $D_A^0(\partial C_A/\partial x)\delta t$ and generates an increase ΔF_A of the mass fraction of A in the zone; since this increase is spread over the distance $\delta\xi$, its value is $\Delta F_A = [D_A^0(\partial C_A/\partial x)\delta t]/\delta\xi = (D_A^0/\dot{\xi})(\partial C_A/\partial x)$. Now ΔF_A is entirely consumed in formation of oxides since the concentration C_A of A in the M phase is zero at the oxidation front; it therefore results, by equation (1), in an increase $\Delta P = (M_P/m_A)(\Delta F_A/\nu)$ of the mass fraction of oxides in the zone $[\xi(t), \xi(t)+\delta\xi]$. Since this zone is free of oxides at time t, the mass fraction of oxides it contains at time $t+\delta t$ is simply

$$P = \Delta P = \frac{M_P}{m_A}\frac{\Delta F_A}{\nu} = \frac{1}{\nu}\frac{M_P}{m_A}\frac{D_A^0}{\dot{\xi}(t)}\frac{\partial C_A}{\partial x}\left[\xi(t)^+,t\right]. \tag{15}$$

The dependence of P upon t in this equation is only apparent, as will be clear from the solution developed below.

3.3 Analytical solution

In Wagner (1959)'s original treatment of the problem, which disregarded both the effect of possibly large fractions of oxides and their role as diffusion barriers, the factors $f(P)$ and $(1-P)f(P)$ were absent from equations (11) and (14). Their presence in this work makes the solution of the problem more difficult, since these terms are unknown *a priori* - the determination of P being an integral part of the problem.

The key to this difficulty is to formally consider, in a first step, the quantity P as known and fixed; the solution may then be developed following the same lines as in the work of Wagner (1959). In a second step, equation (15) will provide, rather than the explicit value of P like in Wagner (1959)'s work, some (nonlinear) equation on this quantity, which will "close the loop".

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[4] The lack of rigor of this reasoning is only apparent; it may be given a completely formal, much heavier but totally rigorous presentation.

Step 1. The position $\xi(t)$ of the oxidation front is looked for in the form

$$\xi(t) = 2\gamma\sqrt{f(P)D_O^0\,t} \tag{16}$$

where γ is a positive constant to be determined. With this notation, the solutions of the diffusion equation (11) of O with conditions $(13)_{1,3}$ plus the requirement that $C_O(x,t)$ be zero at $x = \xi(t)^-$, and of the diffusion equation (12) of A with conditions $(13)_{2,4}$ plus the requirement that $C_A(x,t)$ be zero at $x = \xi(t)^+$, are elementary and read:

$$\begin{cases} \dfrac{C_O(x,t)}{C_O^{\text{surf}}} = 1 - \dfrac{\operatorname{erf}\left[\frac{x}{2\sqrt{f(P)D_O^0\,t}}\right]}{\operatorname{erf}\gamma} & \text{for} \quad 0 \le x \le \xi(t) \\ \dfrac{C_A(x,t)}{C_A^{\text{core}}} = 1 - \dfrac{\operatorname{erfc}\left[\frac{x}{2\sqrt{D_A^0\,t}}\right]}{\operatorname{erfc}\left(\gamma\sqrt{\phi(P)}\right)} & \text{for} \quad \xi(t) \le x < +\infty \end{cases} \qquad \text{where} \quad \phi(P) \equiv f(P)\,\frac{D_O^0}{D_A^0}\,, \tag{17}$$

with erf and erfc denoting the classical error and complementary error functions. Condition (14) then provides the following equation on γ, which implicitly defines this quantity:

$$\frac{e^{\gamma^2}\operatorname{erf}\gamma}{\sqrt{\phi(P)}\;e^{\gamma^2\phi(P)}\;\operatorname{erfc}(\gamma\sqrt{\phi(P)})} = \nu(1-P)\,\frac{m_A}{m_O}\,\frac{C_O^{\text{surf}}}{C_A^{\text{core}}}\,. \tag{18}$$

Step 2. Equation (15) then yields

$$P = \frac{M_P}{m_A}\,\frac{C_A^{\text{core}}}{\nu}\,\frac{e^{-\gamma^2\phi(P)}}{\gamma\sqrt{\pi\phi(P)}\;\operatorname{erfc}\left(\gamma\sqrt{\phi(P)}\right)} \tag{19}$$

where the right-hand side depends upon P through the quantity $\phi(P)$ defined by equation $(17)_3$.

3.4 A useful approximation

The focus of this paper is on the transition from internal to external oxidation. In general, for formation of some external scale of oxides to be possible, the fraction P of oxides in the oxidized zone must be comparable to unity, not much smaller than it. Since in practical situations the core fraction C_A^{core} of A is always small, equation (19) implies that the quantity

$$\frac{e^{-\gamma^2\phi(P)}}{\gamma\sqrt{\phi(P)}\;\operatorname{erfc}\left(\gamma\sqrt{\phi(P)}\right)}$$

must then be much larger than unity. Now using the asymptotic expansion of the function erfc near infinity, available from many sources, one easily sees that this cannot occur for values of the argument $\gamma\sqrt{\phi(P)}$ of order, or much larger than, unity; that is, this argument must be much smaller than unity. Since in practice the quantity $\phi(P)$ defined by equation

$(17)_3$ is large (oxygen diffuses much more quickly than the oxidizable element), this implies that the quantity γ itself must be even smaller.

We therefore introduce the following restrictive hypotheses:

$$\gamma \ll 1 \quad ; \quad \gamma\sqrt{\phi(P)} \ll 1. \tag{20}$$

In equation (18) on γ, one may then use the approximations $e^{\gamma^2} \simeq 1$, $\operatorname{erf}\gamma \simeq \frac{2}{\sqrt{\pi}}\gamma$, $e^{\gamma^2\phi(P)} \simeq 1$, $\operatorname{erfc}(\gamma\sqrt{\phi(P)}) \simeq 1$, leading to the following explicit expression of γ:

$$\gamma \simeq \frac{\nu}{2}(1-P)\,\frac{m_A}{m_O}\,\frac{C_O^{\rm surf}}{C_A^{\rm core}}\,\sqrt{\pi\phi(P)}\,. \tag{21}$$

Equation (19) then yields upon use of the same approximations:

$$P \simeq \frac{M_P}{m_A}\,\frac{C_A^{\rm core}}{\nu}\,\frac{1}{\gamma\sqrt{\pi\phi(P)}} \simeq \frac{2}{\pi\nu^2}\,\frac{1}{(1-P)f(P)}\,\frac{M_P\,m_O}{m_A^2}\,\frac{D_A^0}{D_O^0}\,\frac{(C_A^{\rm core})^2}{C_O^{\rm surf}} \tag{22}$$

where equation $(17)_3$ has been used.

It must finally be noted that in some practical cases, the fraction P of oxides in the oxidized zone is not sufficiently large to warrant full satisfaction of the second of hypotheses (20). As a result, formulae (21), (22) plus those derived below from them, and notably the expression (27) of the critical fraction $P^{\rm crit}$ of oxides, only represent rough approximations. We shall see an example of such a situation in Subsection 4.6 below.

3.5 Transition from internal to external oxidation

Although the nonlinear equation (22) on P differs from those studied in the works of Leblond (2011) and Leblond *et al.* (2013), the discussion of the existence of solutions basically follows the same lines. Define a parameter χ and a function $\overline{f}(P)$ by the formulae

$$\chi \equiv \frac{\pi\nu^2}{2}\,\frac{m_A^2}{M_P\,m_O}\,\frac{D_O^0}{D_A^0}\,\frac{C_O^{\rm surf}}{(C_A^{\rm core})^2} \quad ; \quad \overline{f}(P) \equiv (1-P)f(P). \tag{23}$$

(Note that χ is independent of the unknowns of the problem and completely determined by the data). Then equation (22) takes the form

$$\chi P = \frac{1}{\overline{f}(P)}\,. \tag{24}$$

This equation on P is best discussed graphically, see Figure 4.

When P increases from 0 to 1, the function $1/\overline{f}(P)$ increases from 1 to $+\infty$. (Note that $\overline{f}(0) = f(0) = 1$ since there can be no reduction of diffusion coefficients in the absence of P phase). Therefore equation (24) may have zero, one or two solutions in P, depending on the value of χ. Gradually change the conditions of the problem, making them more

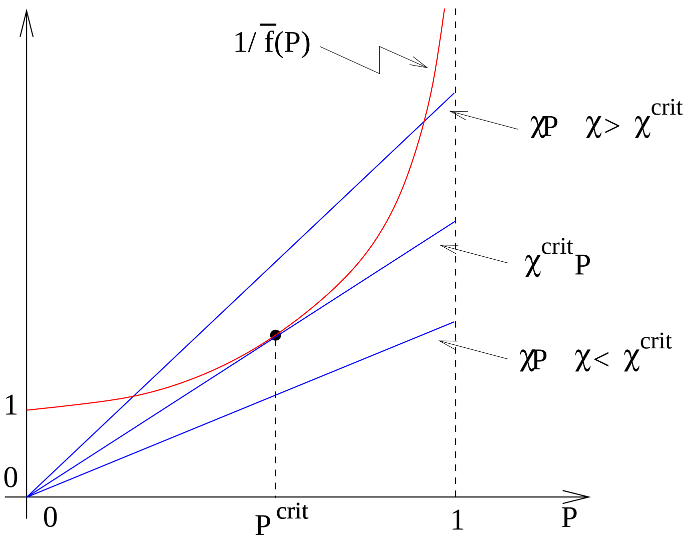

Fig. 4. Graphical discussion of the existence of solutions to equation (24).

and more favorable to external oxidation by gradually increasing the core value $C_A^{\rm core}$ of the concentration of oxidizable element. The definition $(23)_1$ of χ implies that it gradually decreases from infinity.

- When $C_A^{\rm core}$ is very small, χ is very large; the almost vertical straight line of slope χ cuts the curve representing the function $1/\overline{f}\,(P)$ near to the origin, thus defining a solution $P \ll 1$. (The other solution close to unity has no physical relevance since it cannot be reached continuously through some gradual increase of $C_A^{\rm core}$).
- When $C_A^{\rm core}$ increases, the slope of the straight line decreases, so that its first intersection with the curve moves away from the origin. When χ reaches some critical value $\chi^{\rm crit}$, the two points of intersection of the straight line and the curve become identical; P reaches its maximum possible value $P^{\rm crit}$.
- When $C_A^{\rm core}$ becomes sufficiently large for χ to become smaller than $\chi^{\rm crit}$, no solution in P exists any more. The only possible solution must be of a different type, with an infinite concentration of oxides on the surface (external oxidation).

The critical values $\chi^{\rm crit}$ and $P^{\rm crit}$ are determined by the requirement that equation (24) possess a double solution in P:

$$\begin{cases} \chi^{\rm crit} P^{\rm crit} - \dfrac{1}{\overline{f}\,(P^{\rm crit})} & = 0 \\ \dfrac{d}{dP}\left[\chi^{\rm crit} P - \dfrac{1}{\overline{f}\,(P)}\right]_{P=P^{\rm crit}} & = 0 \end{cases} \quad \Rightarrow \quad \begin{cases} \chi^{\rm crit} P^{\rm crit} & = \dfrac{1}{\overline{f}\,(P^{\rm crit})} \\ \chi^{\rm crit} & = -\dfrac{\overline{f}\,'(P^{\rm crit})}{\left[\overline{f}\,(P^{\rm crit})\right]^2} \,. \end{cases}$$

Elimination of $\chi^{\rm crit}$ yields the equation determining the value of $P^{\rm crit}$, from which follows that of $\chi^{\rm crit}$:

$$\begin{cases} \dfrac{\overline{f}\,'(P^{\rm crit})}{\overline{f}\,(P^{\rm crit})} + \dfrac{1}{P^{\rm crit}} = \dfrac{d\left(\ln \overline{f}\right)}{dP}(P^{\rm crit}) + \dfrac{1}{P^{\rm crit}} = 0 \\ \chi^{\rm crit} = \dfrac{1}{P^{\rm crit}\,\overline{f}\,(P^{\rm crit})} \,. \end{cases} \qquad (25)$$

The solution in P^{crit} of equation $(25)_1$ may be calculated analytically provided the expression of the function $f(P)$ is simple enough. For instance, for the expression (5) derived from the simplest assumption that diffusion coefficients are reduced proportionally to the volume fraction of the M phase, equation $(25)_1$ yields, upon a straightforward calculation, the following algebraic equation of the second degree:

$$2\left(\frac{v_P}{v_M}-1\right)(P^{\text{crit}})^2+3P^{\text{crit}}-1=0 \tag{26}$$

where v_P denotes the specific volume of the oxidized P phase. The solution of this equation is (excluding the other solution which is physically meaningless, being either smaller than 0 or larger than 1):

$$P^{\text{crit}}=\frac{-3+\sqrt{8v_P/v_M+1}}{4(v_P/v_M-1)}=\frac{2}{3+\sqrt{8v_P/v_M+1}}\,. \tag{27}$$

The value of χ^{crit} then follows from equation $(25)_2$.

It must be emphasized again that in come cases equation (27) only provides a modestly accurate approximation of P^{crit}, because of lack of satisfaction of the second of hypotheses (20). But its major advantage, in spite of this slight deficiency, lies in its explicitness and simplicity.

3.6 Discussion

The first remark to be made is that somewhat paradoxically, the transition from internal to external oxidation does *not* occur when the fraction P of oxides in the oxidized zone reaches unity, but some *smaller value*. This results from the "avalanche effect" depicted in the Introduction: if oxidation near the surface becomes too important, this reduces the penetration of oxygen into the plate through reduction of its diffusion coefficient, which in turn further enhances oxidation and reduces penetration of oxygen, etc. It must be stressed, however, that this result does *not* mean that the external surface is only partially covered by oxides in the external oxidation regime. Of course, external oxidation implies formation of some superficial scale of oxides which completely covers the surface; but our result implies that the transition from partial to total coverage by oxides does not occur in a smooth way, but abruptly and discontinuously. When the core value C_A^{core} of the fraction of oxidizable element is large enough for the fraction P of oxides to reach its critical value P^{crit}, even an infinitesimal increase of C_A^{core} results in a discontinuous, catastrophic increase of P which only ceases when it reaches unity.

The second remark is that quite remarkably, the value of P^{crit} predicted by equation (27) only depends on the specific volumes of the M and P phases, and is *independent of the other physical parameters of the problem, including the diffusion coefficients and the solubility product.* For the solubility product this is not surprising, insofar as it simply disappears, if sufficiently small, from the basic equations of the problem (11-15); but for the diffusion coefficients the property is far from trivial. In contrast, the critical value of the core fraction C_A^{core} of the oxidizable element, which results from the definition $(23)_1$ of χ and the critical value χ^{crit} of this quantity, equation $(25)_2$, depends on all these parameters and notably the diffusion coefficients.

The third remark pertains to the comparison with the work of Leblond (2011). The value of P^{crit} obtained in that work was

$$\frac{1}{1+\sqrt{v_P/v_M}}\,,$$

which is larger than the value predicted by equation (27); the discrepancy may be notable, as the example given below will show. The difference is due to the fact that the equations used by Leblond (2011) corresponded to Wagner (1959)'s original formulation intrinsically limited to small fractions of P phases, so that the factor $(1-P)$ was absent from both the balance equation $(10)_1$ of oxygen and the condition (14) connecting fluxes at the oxidation front.

The fourth and final remark relates to comparison between the theoretical prediction of the transition and experimental observations. The metallurgical literature is replete with values of the critical value of the core fraction of oxidizable element, for various systems under diverse conditions. Unfortunately, as remarked above, the theoretical estimate of this critical value depends on the diffusion coefficients, which as a rule are known only with a considerable margin of error. Comparisons between experimental and theoretical critical values of C_A^{crit} would therefore be of modest significance, and comparisons of theoretical and experimental values of P^{crit} are much preferable. Unfortunately, as already noted in the Introduction, such experimental values seem to be limited to Rapp (1961)'s old estimate of 0.30 for the critical *volume* fraction of In_2O_3 for the $O/In/In_2O_3$ system in an Ag matrix. The specific volumes of Ag and In_2O_3 are $v_M = 95 \times 10^{-6}\,\text{m}^3\,\text{kg}^{-1}$ and $v_P = 139 \times 10^{-6}\,\text{m}^3\,\text{kg}^{-1}$, respectively. For these values equation (27) predicts a critical *mass* fraction of In_2O_3 of 0.30, corresponding to a *volume* fraction of 0.38, in reasonable agreement with Rapp (1961)'s value of 0.30. In contrast Leblond (2011)'s estimate of the critical mass fraction of In_2O_3 amounts to 0.45, corresponding to a volume fraction of 0.55; this value is almost twice larger than that of Rapp (1961). The improvement brought to the prediction of the transition by use of a diffusion/precipitation model incorporating possible large fractions of P phases, such as that of Section 2, is therefore clear.

4 Semi-analytical solution of the oxidation problem for an oxide with a nonzero solubility product

The theoretical treatment of the problem of the transition from internal to external oxidation expounded in the preceding Section, based on the model of Section 2 including the possibility of large fractions of P phases, may be regarded as satisfactory. However this treatment was limited to the case of an oxide with an infinitesimally small solubility product K. As mentioned in the Introduction, whereas this condition of smallness is reasonably satisfied for some systems like $O/Al/Al_2O_3$ in a Fe matrix, it is *not* for some others like O/Mn/MnO in a Fe matrix. It is therefore necessary to extend the treatment to finite, nonzero values of K.

The mathematical analysis here will extend that of Huin *et al.* (2005) of a simpler version of the problem accounting for neither the reduction of diffusion coefficients due to presence of oxides nor the effect of possibly large fractions of P phases. Introducing such effects will result in considerable extra complexities. In addition, the new solution will exhibit some qualitatively new features, as will be seen.

4.1 Presentation of the new problem

Many features of the problem for a nonzero K are similar to those for a zero K. Such features include diffusion of O toward the interior of the plate, diffusion of A toward its exterior, and formation of molecules of formula OA_ν. But the nonzero value of K implies that O and A can now coexist in the M phase. As a result, the zone where oxidation occurs at a given time no longer reduces to a point, but *extends over some region*; as a consequence *the fraction P of oxides now depends on position and time.* (Recall that these two properties are connected, as was shown in Subsection 3.1).

In theory, the oxidized region extends from the surface of the plate to some *a priori* unknown position; it does not extend to infinity since there is no oxygen there. However, assuming that it *does*, that is that the condition $C_O C_A^\nu = K$ is satisfied everywhere, only introduces a minor error; indeed the value of the fictitious core fraction of O deduced from this equality, $C_O^{\mathrm{core}} \equiv K/(C_A^{\mathrm{core}})^\nu$, is in practice "close to zero" in the sense of being much smaller than the value C_O^{surf} imposed on the surface. *We shall therefore make this assumption in the sequel*, thereby simplifying the treatment by eliminating the need for determination of the endpoint of the oxidized zone, without significantly altering the results.

It will also be assumed that *the reduction of diffusion coefficients, due to the presence of oxides acting as barriers, may be different for O and A*; the importance of such an additional "degree of freedom" of the model will be clear in the sequel. This assumption is physically plausible since the extent of the reduction, for a given value of P, depends on the shape of the individual oxides, see formula (6); and the oxides formed close to the surface (where O chiefly diffuses) and deeper in the sheet (where A chiefly diffuses) are precisely bound to assume different shapes - flat ellipsoids near the surface versus spheres farther away.

4.2 Equations of the new problem

In order to lighten the appearance of equations below, we introduce the following notations:

$$\alpha \equiv \frac{m_O}{M_P} \quad ; \quad \beta \equiv \frac{m_A}{M_P} \, . \tag{28}$$

The general mass balance equations (1) then simply read, for elements O and A respectively:

$$\begin{cases} F_O = (1-P)C_O + \alpha P \\ F_A = (1-P)C_A + \beta\nu P. \end{cases} \tag{29}$$

Also, $f_O(P)$ and $f_A(P)$ denoting - like in equation (4) - the functions characterizing the respective reductions of the diffusion coefficients of O and A, we define - like in equation $(23)_2$ - the functions

$$\begin{cases} \overline{f_O}(P) \equiv (1-P)f_O(P) \\ \overline{f_A}(P) \equiv (1-P)f_A(P). \end{cases} \tag{30}$$

With these notations the general diffusion equations (7) take the following form:

$$\begin{cases} \dfrac{\partial F_O}{\partial t} = \dfrac{\partial}{\partial t}\left[(1-P)C_O + \alpha P\right] \ = D_O^0 \dfrac{\partial}{\partial x}\left[\overline{f_O}(P)\dfrac{\partial C_O}{\partial x}\right] \\ \dfrac{\partial F_A}{\partial t} = \dfrac{\partial}{\partial t}\left[(1-P)C_A + \beta\nu P\right] = D_A^0 \dfrac{\partial}{\partial x}\left[\overline{f_A}(P)\dfrac{\partial C_A}{\partial t}\right]. \end{cases} \tag{31}$$

These equations are completed by the condition

$$C_O C_A^\nu = K \tag{32}$$

expressing the hypothesis of local thermodynamic equilibrium with oxides present everywhere in the sheet, as discussed above.

Finally the initial and boundary conditions read

$$\begin{cases} C_O = C_O^{\text{core}} \equiv \frac{K}{(C_A^{\text{core}})^\nu} & \text{for } 0 < x < +\infty,\ t = 0 \\ C_A = C_A^{\text{core}} & \text{for } 0 < x < +\infty,\ t = 0 \end{cases} \tag{33}$$

and

$$\begin{cases} C_O = C_O^{\text{surf}} & \text{for } x = 0,\ 0 \le t < +\infty \\ C_A = C_A^{\text{core}} & \text{for } x \to +\infty,\ 0 \le t < +\infty. \end{cases} \tag{34}$$

4.3 Semi-analytical solution

Like in the case of an infinitesimally small K, we shall look for a solution depending on x and t only through the combination $x/\sqrt{t}$. More precisely we define a new variable u by the formula

$$u \equiv \frac{x}{2\gamma\sqrt{D_O^0\, t}} \tag{35}$$

where γ is an *a priori* free positive parameter, the value of which will be fixed later. This parameter resembles, though it is not identical to, that defined by equation (16) in the case of an infinitesimally small K. Its role is to perform an arbitrary homothetical transformation of space, permitting to always shrink or expand that "interesting" part of the x-axis where the solution varies significantly, to the same fixed part of the u-axis.

All unknowns being considered as functions of u from now on, simple (though tedious) calculations show that the diffusion equations (31) reduce to

$$\begin{cases} \overline{f_O}(P)C_O'' + 2\gamma^2 u(1-P)C_O' + \left[\overline{f_O}'(P)C_O' + 2\gamma^2 u(\alpha - C_O)\right] P' & = 0 \\ \overline{f_A}(P)C_A'' + 2\gamma^2 \psi u(1-P)C_A' + \left[\overline{f_A}'(P)C_A' + 2\gamma^2 \psi u(\beta\nu - C_A)\right] P' & = 0 \end{cases} \quad , \ \psi \equiv \frac{D_O^0}{D_A^0}, \tag{36}$$

where the symbols $'$ and $''$ denote first- and second-derivatives with respect to u, respectively - except when applied to the functions $\overline{f_O}$ and $\overline{f_A}$, for which they of course denote derivatives with respect to P. But the variable C_A is completely tied to C_O through equation (32); hence equation $(36)_2$ may be rewritten in terms of C_O and its derivatives. The result reads:

$$\begin{aligned} &\overline{f_A}(P)\left[C_O'' - \left(1 + \frac{1}{\nu}\right)\frac{C_O'^2}{C_O}\right] + 2\gamma^2\psi u(1-P)C_O' \\ &+ \left[\overline{f_A}'(P)C_O' + 2\gamma^2\psi\nu u\left(1 - \beta\nu\left(\frac{C_O}{K}\right)^{1/\nu}\right)C_O\right]P' = 0. \end{aligned} \tag{37}$$

Equations $(36)_1$ and (37) are coupled, nonlinear ordinary differential equations (ODEs) which both involve the unknowns C_O, C_O', C_O'', P and P'. Unfortunately they do not provide separate and explicit expressions of the highest-order derivatives, C_O'' and P'. But this can easily be remedied by eliminating P' between these equations; the output is an explicit expression of C_O'' in the form of a fraction:

$$C_O'' = \frac{N(C_O, C_O', P)}{D(C_O, C_O', P)} \tag{38}$$

where [5]

$$\begin{cases} N(C_O, C_O', P) \equiv \left[\overline{f_O}'(P)C_O' + 2\gamma^2 u(\alpha - C_O)\right]\left[\overline{f_A}(P)\left(1+\frac{1}{\nu}\right)\frac{C_O'^2}{C_O} - 2\gamma^2\psi u(1-P)C_O'\right] \\ \qquad\qquad\qquad + 2\gamma^2 u(1-P)C_O'\left[\overline{f_A}'(P)C_O' + 2\gamma^2\psi\nu u\left(1 - \beta\nu\left(\frac{C_O}{K}\right)^{1/\nu}\right)C_O\right] \\ D(C_O, C_O', P) \equiv \left[\overline{f_O}'(P)\overline{f_A}(P) - \overline{f_O}(P)\overline{f_A}'(P)\right]C_O' \\ \qquad\qquad\qquad + 2\gamma^2 u\left[\overline{f_A}(P)(\alpha - C_O) + \psi\nu\overline{f_O}(P)\left(\beta\nu\left(\frac{C_O}{K}\right)^{1/\nu} - 1\right)C_O\right]. \end{cases} \tag{39}$$

Once C_O'' is known, P' is easily deduced from equation $(36)_1$:

$$P' = -\frac{\overline{f_O}(P)C_O'' + 2\gamma^2 u(1-P)C_O'}{\overline{f_O}'(P)C_O' + 2\gamma^2 u(\alpha - C_O)} = -\frac{\overline{f_O}(P)\frac{N(C_O,C_O',P)}{D(C_O,C_O',P)} + 2\gamma^2 u(1-P)C_O'}{\overline{f_O}'(P)C_O' + 2\gamma^2 u(\alpha - C_O)}. \tag{40}$$

---

[5] The expression of the numerator $N(C_O, C_O', P)$ here may be developed in a more explicit way, but with no gain in either formal simplicity or physical insight.

Equations (38) and (40) are coupled, nonlinear ODEs on the functions $C_O(u)$ and $P(u)$, of second order in C_O and first order in P.

4.4 Asymptotic solution near the surface

We shall now see that some restrictions on the given parameters of the problem are needed in order to warrant a physically reasonable solution near the surface of the plate ($u \to 0^+$).

In order to be reasonable, the solution must satisfy the following properties:

- $C'_O(u = 0)$ *should be finite* (since it is tied to the input flux of oxygen which cannot physically be infinite);
- $P(u = 0)$ *should be finite* (since it cannot exceed unity by definition).

Let us assume these properties to be satisfied, and examine whether or not a contradiction arises with the expressions (38) and (40) of C''_O and P'.

The first task is to examine the expression $(39)_2$ of the denominator $D(C_O, C'_O, P)$ in equation (38), and see whether it may or may not vanish in the limit $u \to 0^+$. In this limit $D(C_O, C'_O, P)$ reduces to $\left[\overline{f_O}'(P)\overline{f_A}(P) - \overline{f_O}(P)\overline{f_A}'(P)\right] C'_O$; this expression is zero if, and only if,

$$\begin{aligned}
&\overline{f_O}'(P)\overline{f_A}(P) - \overline{f_O}(P)\overline{f_A}'(P) = 0 \quad &\Leftrightarrow \quad &\frac{\overline{f_O}'(P)}{\overline{f_O}(P)} - \frac{\overline{f_A}'(P)}{\overline{f_A}(P)} = 0 \quad \Leftrightarrow \\
&\ln[\overline{f_O}(P)] - \ln[\overline{f_A}(P)] = Cst. \quad &\Leftrightarrow \quad &\frac{\overline{f_O}(P)}{\overline{f_A}(P)} = Cst.
\end{aligned}$$

But the last constant can only be unity then because of the conditions $\overline{f_O}(0) = \overline{f_A}(0) = 1$ (there is no reduction of the diffusion coefficients in the absence of oxides); which entails that necessarily $\overline{f_O}(P) = \overline{f_A}(P)$. The conclusion is that *in the limit $u \to 0^+$, $D(C_O, C'_O, P)$ is zero if, and only if, the functions $\overline{f_O}$ and $\overline{f_A}$ (or equivalently the functions f_O and f_A) are identical.*

It is thus necessary to distinguish between two cases:

- *Case 1: the functions f_O and f_A are identical.* Then the denominator $D(C_O, C'_O, P)$ is zero in the limit $u \to 0^+$, so that it is of order 1 in u (see equation $(39)_2$). Hence by equation (38) where $N(C_O, C'_O, P)$ is finite in the limit $u \to 0^+$, C''_O is asymptotically of the form $Cst./u$, so that C'_O is of the form $Cst. \times \ln u$ and diverges to infinity for $u \to 0^+$. This type of solution contradicts the hypothesis made of a finite C'_O at $u = 0$, and is physically unacceptable because it implies an infinite input flux of oxygen on the surface. (In addition, equation (40) then implies that P' diverges like $\frac{1}{u \ln u}$ and P like $\ln(-\ln u)$, which is equally contradictory with the hypotheses made and no more physically acceptable).
- *Case 2: the functions f_O and f_A are distinct.* Then the denominator $D(C_O, C'_O, P)$ does not vanish in the limit $u \to 0^+$, so that C''_O goes to a finite constant in this limit; it

follows from integration that C'_O also goes to some finite value, as desired. Furthermore by equation (40), P' goes to a finite limit and consequently so does also P. These properties are compatible with the hypotheses made and physically reasonable.

The conclusion is that *the functions f_O and f_A, depicting the reduction of the diffusion coefficients of O and A due to presence of oxides acting as barriers, must be assumed to be different for the solution to make sense.* (This point will be further commented below). Such a hypothesis will be made in the sequel.

4.5 Numerical algorithm

The formidable complexity of the system (38, 40) of coupled nonlinear ODEs dashes any hope of solving them analytically. However they are expressed in a format perfectly fit for numerical integration using standard methods, for instance that of Runge-Kutta of order 4. With such a method, one must prescribe the values of C_O, C'_O and P at $u = 0$; integration then yields the values of these functions up to large values of u approximating infinity.

However one may take advantage here of the extra degree of freedom brought into the equations by introducing the free parameter γ in the definition (35) of the variable u. Indeed, instead of fixing γ and varying $C'_O(u = 0)$, one may fix $C'_O(u = 0)$ and vary γ; the value $C'_O(u = 0) = -1$, more specifically, will be used in all simulations discussed below. The advantage of such a procedure and value is that they warrant that the region of the u-axis where C_O (and consequently P) vary significantly, will always be of size comparable to unity, thereby permitting to use a single mesh for all simulations.

One difficulty, however, is that among the three quantities $C_O(u = 0)$, γ and $P(u = 0)$, only the first one, $C_O(u = 0) = C_O^{\mathrm{surf}}$, is known and prescribed by the data of the problem. The other two, γ and $P(u = 0)$, are not; but two quantities are known instead at infinity: $P(u = +\infty)$ which must be zero - there are no oxides deep in the sheet - and $C_A(u = +\infty) = [K/C_O(u = +\infty)]^{1/\nu}$, which must be identical to the value C_A^{core} imposed by the grade of the steel.

Let us momentarily forget about the satisfaction of the condition $C_A(u = +\infty) = C_A^{\mathrm{core}}$, and assume that $P(u = 0)$ is fixed. The problem then reduces to finding the value of γ warranting satisfaction of the condition $P(u = +\infty) = 0$. Since this just means adjusting a single, scalar parameter, it can be done by various standard methods; the most robust being a simple dichotomy, with each step consisting of a numerical integration of equations (38, 40) yielding the value of $P(u = +\infty)$ for a given γ.

To finally fulfill the condition $C_A(u = +\infty) = C_A^{\mathrm{core}}$, one could think of adjusting the value of $P(u = 0)$ in a similar way. However, for a given, fixed value of C_O^{surf}, a simpler solution consists of performing simulations for various values of $P(u = 0)$ (with a suitable adjustment of γ every time, as just discussed). In this way one gets, for the value of C_O^{surf} considered, a discrete set of pairs $[P(u = 0), C_A(u = +\infty)]$ which easily permits to plot C_A^{core} versus $P(u = 0)$ or $P(u = 0)$ versus C_A^{core}, depending on one's taste. (In fact the plot of C_A^{core} versus $P(u = 0)$ will reveal more convenient for the study of the transition from internal to external oxidation, as will be seen in the Subsection 4.6).

To summarize, the algorithm adopted consists of the following elements, ordered "top to bottom":

- for a given value of C_O^{surf}, a set of calculations of C_A^{core} as a function of $P(u = 0)$;
- for each such calculation, a dichotomy on the parameter γ aimed at fulfilling the condition $P(u = +\infty) = 0$;
- for each iteration of such a dichotomy, numerical integration from zero to "infinity" of the nonlinear ODEs (38, 40) using the given values of C_O^{surf}, γ and $P(u = 0)$.

4.6 Numerical results and discussion

As an example, we consider the case of the system O/Mn/MnO (having thus $\nu = 1$) in a Fe matrix, at a temperature of 800°C. The diffusion and precipitation constants of this sytem are taken from (Oikawa, 1982) and the (Thermodata, 2005) data bank; they are given in Table 1.

m_O (g)	m_{Mn} (g)	M_{MnO} (g)	D_O^0 (μm^{2}s^{-1})	D_{Mn}^0 (μm^{2}s^{-1})	K (ppm^2)
15.999	54.938	70.937	8.02	9.09×10^{-4}	7.21

Table 1
Diffusion and precipitation constants of the system O/Mn/MnO in a Fe matrix.

In addition, the data required for the definition of the functions f_O and $f_A \equiv f_{Mn}$, depicting the reduction of diffusion coefficients by oxides acting as barriers, are listed in Table 2.

$v_{MnO} \equiv v_P$ (m^3 kg^{-1})	$v_{Fe} \equiv v_M$ (m^3 kg^{-1})
0.1862×10^{-3}	0.1272×10^{-3}

Table 2
Specific volumes for the system O/Mn/MnO in a Fe matrix.

In all simulations discussed below, the function f_O depicting the reduction of D_O is considered to be given by the simple formula (5), whereas the function f_{Mn} pertaining to the reduction of $D_A \equiv D_{Mn}$ is taken as unity (no reduction at all). The larger reduction of D_O, as compared to that of D_{Mn}, is in line with the remark made in Subsection 4.1, about the different shapes of the oxides acting as obstacles to the diffusion of oxygen and the oxidizable element.

Various values of the mass concentration C_O^{surf} of oxygen imposed on the surface are envisaged: 0.01, 0.02, 0.03, 0.1, 0.3, 0.5 and 1 ppm. It is worth mentioning here that this value, together with that of $C_A^{\text{core}} \equiv C_{Mn}^{\text{core}}$, determines whether the solubility product must be considered as "small" or "large": in order to decide about the "magnitude" of K, the dimensionless number that must be compared to unity is $\frac{K}{C_O^{\text{surf}} C_{Mn}^{\text{core}}}$. If it is very much smaller than unity, the solution of Section 3 for an infinitesimally small K may be deemed applicable. But the effects upon this ratio of a decrease of K and an increase of C_O^{surf} are strictly identical. Thus for a fixed K, like in the simulations discussed hereafter, the larger the value of C_O^{surf}, the more the solution of Section 3 may be expected to be applicable.

This aspect is plainly illustrated in Figure 5, which shows the distributions of C_O, C_{Mn} and P at time $t = 100\,\mathrm{s}$, for two values of C_O^{surf} and the same value of P on the surface, $P(u = 0) = 0.31$. (This would exactly be the value of the critical fraction of oxides corresponding to the transition from internal to external oxidation, *if* K were infinitesimally small; see the discussion below). For $C_O^{\mathrm{surf}} = 1\,\mathrm{ppm}$, all three distributions exhibit features analogous, though not completely identical, to those for an infinitesimally small K, see Figure 2. On the other hand, for $C_O^{\mathrm{surf}} = 0.1\,\mathrm{ppm}$, these distributions are markedly different: O and Mn coexist over some notable distance and P is no longer uniform within the oxidized zone.

Figure 6, which displays C_{Mn}^{core} versus the surface fraction of oxides $P(u = 0)$ for various values of C_O^{surf}, permits to discuss the existence of a sharp transition from internal to external oxidation and the conditions governing such a transition. The following remarks are in order.

- Consider first the three highest values of C_O^{surf}, 1, 0.5 and 0.3 ppm, for which the solution does not differ too much from that of Section 3 for an infinitesimally small K. For these values, the curve representing C_{Mn}^{core} versus $P(u = 0)$ exhibits a maximum. Therefore, if one gradually increases C_{Mn}^{core} from zero, the point $[P(u = 0), C_{Mn}^{\mathrm{core}}]$ follows the left portion of the curve from the origin, until the maximum is reached; for values of C_{Mn}^{core} larger than the maximum value, no solution to the equations of internal oxidation can be found, meaning that a switch from internal to external oxidation must necessarily occur. This is exactly the same situation as in Section 3, albeit presented in somewhat different geometric terms. (Note that the portion of the curve located to the right of the maximum, where C_{Mn}^{core} becomes a decreasing function of $P(u = 0)$, has no physical existence since it cannot be reached by continuously increasing C_{Mn}^{core}).
- The surface fraction $P(u = 0)$ of MnO corresponding to the maximum, when it exists ($C_O^{\mathrm{surf}} = 1$, 0.5 and 0.3 ppm), is the same no matter the value of C_O^{surf}. This feature is in agreement with the expression (27) of P^{crit} for an infinitesimally small K, which predicts no effect of C_O^{surf} upon this critical value. On the other hand the maximum value of C_{Mn}^{core} is clearly an increasing function of C_O^{surf}. This is again in agreement with the results of Section 3: equation $(25)_2$ predicts a value of χ^{crit} independent of C_O^{surf} like P^{crit}, but the expression $(23)_1$ of χ then implies that the critical value of C_{Mn}^{core} is proportional to the square root of C_O^{surf}.
- The theoretical value of P^{crit} for an infinitesimal K deduced from equation (27), with the data provided in Table 2, is 0.31. But numerically, the surface fraction $P(u = 0)$ of oxides corresponding to the maximum of C_{Mn}^{core} when it exists ($C_O^{\mathrm{surf}} = 1$, 0.5 and 0.3 ppm), is somewhat larger, in the range $0.39 - 0.41$. This is *not* because the condition $\frac{K}{C_O^{\mathrm{surf}} C_{Mn}^{\mathrm{core}}} \ll 1$ is not met, but rather because equation (27) is based on the restrictive assumptions (20), the second of which is poorly satisfied in the cases considered.[6] On

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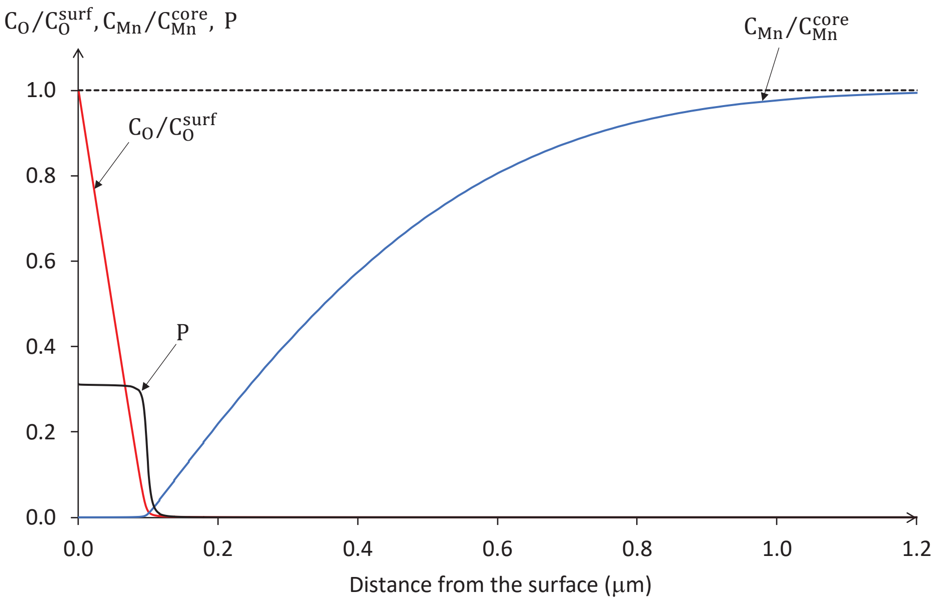
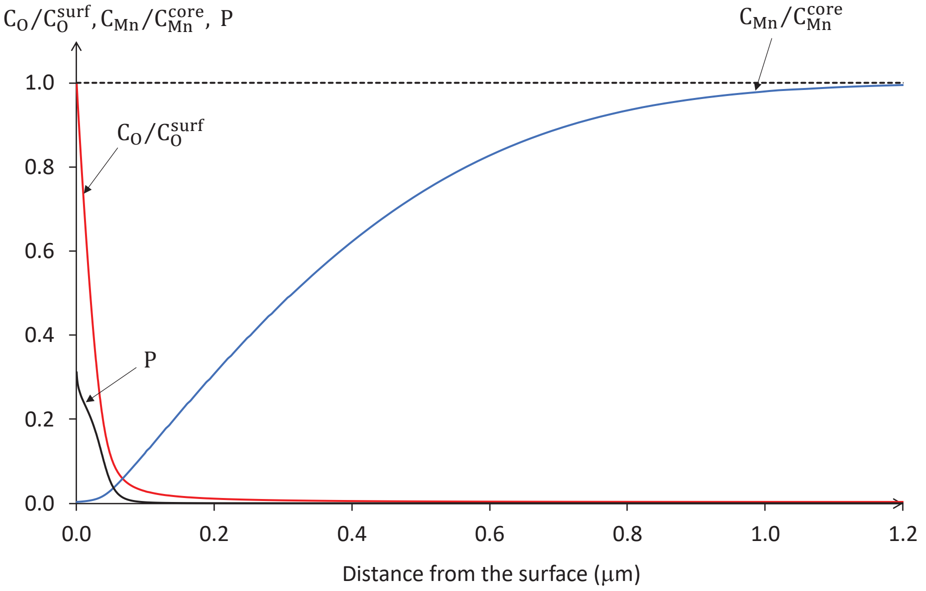
[6] Additional calculations have been performed with very small values of K and C_O^{surf}, implying full satisfaction of both assumptions (20); the theoretical value $P^{\mathrm{crit}} \simeq 0.31$ is then completely



(a) $C_O^{\rm surf} = 1\,{\rm ppm}$



(b) $C_O^{\rm surf} = 0.1\,{\rm ppm}$

Fig. 5. Mass concentrations of O and Mn and mass fraction of MnO at $t = 100\,{\rm s}$, for two values of $C_O^{\rm surf}$ and the same surface value of P, $P(u = 0) = 0.31$.

the other hand, the theoretical critical values of $C_{Mn}^{\rm core}$ deduced from equations $(23)_1$ and $(25)_2$ are 6.93×10^4, 4.90×10^4 and 3.80×10^4 ppm for $C_O^{\rm surf} = 1$, 0.5 and 0.3 ppm respectively, versus 5.99×10^4, 4.46×10^4 and 3.60×10^4 ppm for the maximum values of $C_{Mn}^{\rm core}$ found numerically; the agreement is thus better for this quantity.

- For the smallest values of $C_O^{\rm surf}$, 0.03, 0.02 and 0.01 ppm, the curve representing $C_{Mn}^{\rm core}$ versus $P(u = 0)$ has no maximum, meaning that a solution of the equations of internal oxidation can always be found, however large the value of $C_{Mn}^{\rm core}$. In other words, there is no sharp transition from internal to external oxidation; total coverage of the surface of

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recovered numerically.

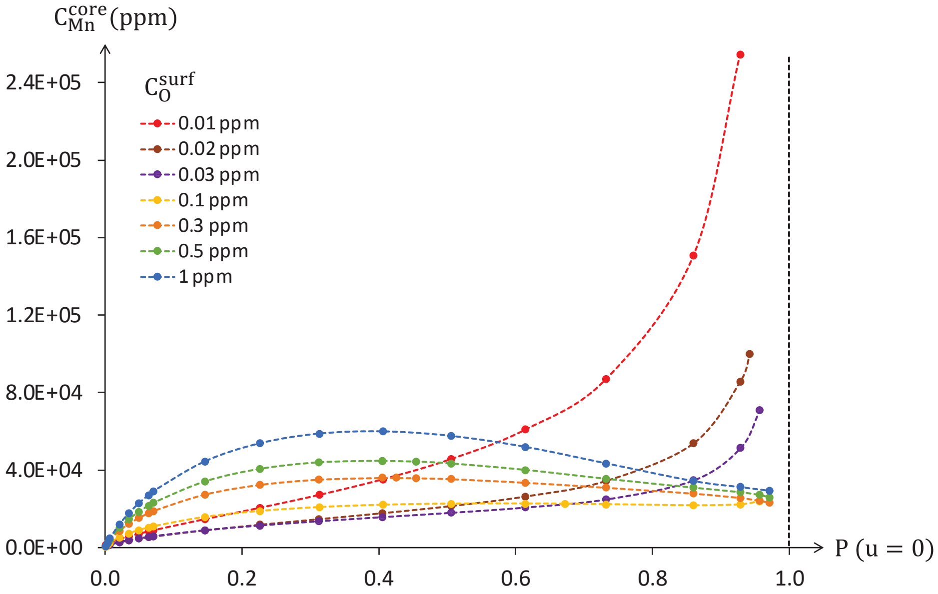

Fig. 6. Core fraction of Mn versus surface fraction of MnO, for various values of C_O^{surf}.

the sheet can only be achieved through some continuous, potentially unlimited increase of C_{Mn}^{core}.

In spite of their physical and practical interest, these results raise several issues specific to the case of a nonzero K.

- The prediction of absence, in some cases, of a sharp transition from internal to external oxidation, is surprising although admittedly not altogether physically impossible.
- In order to get reasonable model predictions, we had no choice but to assume different functions f_O, f_{Mn} for the reduction of the diffusion coefficients of O and Mn, see Subsection 4.4. Now although such a hypothesis is reasonable in many cases (as explained above), one may imagine situations where the reduction of diffusion coefficients is the same for both elements (in the absence of significant differences in shape of oxides located at different depths). In such situations the divergence of some quantities near the surface (see Subsection 4.4) is a clear indication of the physical breakdown of the equations of the model.
- A final issue pertains to boundary conditions. Because of the input flux of O, the derivative $\partial C_O/\partial x$ is negative on the surface; the relation $C_O C_{Mn} = K$ then implies that the derivative $\partial C_{Mn}/\partial x$ is positive, whence a nonzero output flux of Mn. But the usual assumption in problems of this type is that the flux of the oxidizable element on the surface is nil.

  The assumption of zero flux of Mn is admittedly criticizable insofar as one may imagine mechanisms leading to losses of atoms of Mn into the outer atmosphere; but then such losses should be governed by parameters pertaining to these mechanisms, not by the input flux of O. Stated differently, the problem is more with the *number* of boundary conditions than with their *type*: the hypothesis of instantaneous local thermodynamic equilibrium implies that there can only be *one* (the surface values of C_{Mn} and $\partial C_{Mn}/\partial x$ being determined by those of C_O and $\partial C_O/\partial x$), whereas one naturally expects *two* independent boundary conditions to be required for *two* diffusing species.

It may be remarked that all three issues are related to phenomena occurring on or near the surface of the sheet, which is an indication that the equations of the model may become inadequate there. But what distinguishes the vicinity of the surface from the interior of the sheet is that all processes are quicker here than there (because of larger concentration gradients). This suggests that the root of the difficulties may be that these processes are too quick for local thermodynamic equilibrium to prevail. The next Section will be devoted to some preliminary investigation of this idea.

5 Precipitation kinetics: the solution to the issues raised?

5.1 Generalities

In this Section, we shall modify the model by replacing the hypothesis of instantaneous local thermodynamic equilibrium through some kinetic equation for the precipitation of oxides. The aim is to see whether or not this modification may be hoped to solve the difficulties evidenced in Subsection 4.6, in the case of an oxide with a nonzero solubility product.

More specifically, we shall focus on the issue of the nonzero output flux of oxidizable element on the surface. The aim will *not* be to develop a realistic, necessarily complex kinetic model, such a task being left for future work. It will just be to show, using an elementary, inevitably rough model, how introduction of some kinetics of precipitation does appear to solve the issue. The proof will be based on examination of the mathematical character of the new equations.

Because of the essentially qualitative character of the proof, a number of hypotheses will be made so as to avoid unnecessary complexities in the model:

- Two elements only, O and A, and a single oxide of formula OA (that is with $\nu = 1$ with the notations of Sections 3 and 4), will be considered.
- The effect of possible large fractions of the P phase will be disregarded, together with the reduction of diffusion coefficients due to presence of this phase.
- Kinetics of precipitation of oxides will be governed by a classical Johnson-Mehl-Avrami equation with an exponent of unity, depicting a simple exponential relaxation toward the state of local thermodynamic equilibrium.
- The *equilibrium fraction of P phase* appearing in this kinetic equation will be assumed to be nonzero everywhere and at all instants; this is true provided the total fractions of elements are large enough.[7]

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[7] Note the similarity with the hypothesis introduced in Subsection 4.1 (where instantaneous local thermodynamic equilibrium was assumed) that $C_O C_A^{\nu} = K$ - *not* $\leq K$ - everywhere and at all instants.

5.2 *Diffusion/precipitation equations including precipitation kinetics*

With the hypotheses made, the balance equations (1) reduce to

$$\begin{cases} F_O = C_O + \frac{m_O}{M_P} P \\ F_A = C_A + \frac{m_A}{M_P} P \end{cases} \tag{41}$$

and the diffusion equations (7) to

$$\begin{cases} \dfrac{\partial F_O}{\partial t} = D_O^0 \dfrac{\partial^2 C_O}{\partial x^2} \\ \dfrac{\partial F_A}{\partial t} = D_A^0 \dfrac{\partial^2 C_A}{\partial x^2} \, . \end{cases} \tag{42}$$

However the condition (8) expressing instantaneous local thermodynamic equilibrium is replaced here by the kinetic equation

$$\frac{\partial P}{\partial t} = \tau^{-1} \left(P^{\mathrm{eq}} - P \right) , \tag{43}$$

where τ denotes some characteristic time (material parameter), and P^{eq} the *local equilibrium fraction of P phase* defined by the local chemical composition, that is the total fractions of elements F_O and F_A. This quantity, together with the corresponding equilibrium concentrations of elements C_O^{eq} and C_A^{eq}, are defined by the following equations:

$$\begin{cases} F_O & = C_O^{\mathrm{eq}} + \frac{m_O}{M_P} P^{\mathrm{eq}} \\ F_A & = C_A^{\mathrm{eq}} + \frac{m_A}{M_P} P^{\mathrm{eq}} \\ C_O^{\mathrm{eq}} C_A^{\mathrm{eq}} & = K. \end{cases} \tag{44}$$

Note the sign = instead of ≤ in the last equation, in agreement with the hypothesis introduced in Subsection 5.1 of a nonzero P^{eq} everywhere and at all instants.

5.3 *Reduction to a system of coupled nonlinear diffusion equations*

We shall now show that the above equations can be reduced to a system of coupled, nonlinear diffusion equations on the sole unknowns C_O and C_A.

Combining first equations (41), (42) and (43), we get

$$\begin{cases} \dfrac{\partial C_O}{\partial t} + \dfrac{m_O}{M_P} \dfrac{\partial P}{\partial t} = D_O^0 \dfrac{\partial^2 C_O}{\partial x^2} \\ \dfrac{\partial C_A}{\partial t} + \dfrac{m_A}{M_P} \dfrac{\partial P}{\partial t} = D_A^0 \dfrac{\partial^2 C_A}{\partial x^2} \end{cases} \Rightarrow \begin{cases} \dfrac{\partial C_O}{\partial t} = D_O^0 \dfrac{\partial^2 C_O}{\partial x^2} - \dfrac{m_O}{M_P} \tau^{-1} \left(P^{\mathrm{eq}} - P \right) \\ \dfrac{\partial C_A}{\partial t} = D_A^0 \dfrac{\partial^2 C_A}{\partial x^2} - \dfrac{m_A}{M_P} \tau^{-1} \left(P^{\mathrm{eq}} - P \right) . \end{cases}$$

But combining equations $(41)_1$ and $(44)_1$, $(41)_2$ and $(44)_2$, one sees that

$$P^{\mathrm{eq}} - P = \frac{M_P}{m_O}\,(C_O - C_O^{\mathrm{eq}}) = \frac{M_P}{m_A}\,(C_A - C_A^{\mathrm{eq}})\,; \tag{45}$$

hence the preceding equations may be rewritten in the form

$$\begin{cases} \dfrac{\partial C_O}{\partial t} = D_O^0 \dfrac{\partial^2 C_O}{\partial x^2} - \tau^{-1}\,(C_O - C_O^{\mathrm{eq}}) \\ \dfrac{\partial C_A}{\partial t} = D_A^0 \dfrac{\partial^2 C_A}{\partial x^2} - \tau^{-1}\,(C_A - C_A^{\mathrm{eq}})\,. \end{cases} \tag{46}$$

It remains to calculate the equilibrium concentrations C_O^{eq}, C_A^{eq} in terms of the actual concentrations C_O, C_A. By equations (45) and $(44)_3$, they satisfy the following relations:

$$\begin{cases} \frac{C_O^{\mathrm{eq}}}{m_O} - \frac{C_A^{\mathrm{eq}}}{m_A} = \frac{C_O}{m_O} - \frac{C_A}{m_A} \\ C_O^{\mathrm{eq}} C_A^{\mathrm{eq}} \quad = K. \end{cases} \tag{47}$$

Defining $\overline{C}_O^{\mathrm{eq}} \equiv C_O^{\mathrm{eq}}/m_O$ and $\overline{C}_A^{\mathrm{eq}} \equiv -C_A^{\mathrm{eq}}/m_A$, one sees that these equations provide the values of the sum of $\overline{C}_O^{\mathrm{eq}}$ and $\overline{C}_A^{\mathrm{eq}}$, $\frac{C_O}{m_O} - \frac{C_A}{m_A}$, and their product, $-\frac{K}{m_O m_A}$; it follows that these quantities are the positive and negative roots, respectively, of the algebraic equation of the second degree

$$X^2 - \left(\frac{C_O}{m_O} - \frac{C_A}{m_A}\right) X - \frac{K}{m_O m_A} = 0.$$

Solving this equation, one gets

$$\begin{cases} \overline{C}_O^{\mathrm{eq}} = \frac{C_O^{\mathrm{eq}}}{m_O} \quad = \frac{1}{2}\left[\frac{C_O}{m_O} - \frac{C_A}{m_A} + \sqrt{\left(\frac{C_O}{m_O} - \frac{C_A}{m_A}\right)^2 + \frac{4K}{m_O m_A}}\right] \\ \overline{C}_A^{\mathrm{eq}} = -\frac{C_A^{\mathrm{eq}}}{m_A} = \frac{1}{2}\left[\frac{C_O}{m_O} - \frac{C_A}{m_A} - \sqrt{\left(\frac{C_O}{m_O} - \frac{C_A}{m_A}\right)^2 + \frac{4K}{m_O m_A}}\right], \end{cases}$$

from which follows that

$$\frac{C_O - C_O^{\mathrm{eq}}}{m_O} = \frac{C_A - C_A^{\mathrm{eq}}}{m_A} \equiv \theta(C_O, C_A) \equiv \frac{1}{2}\left[\frac{C_O}{m_O} + \frac{C_A}{m_A} - \sqrt{\left(\frac{C_O}{m_O} - \frac{C_A}{m_A}\right)^2 + \frac{4K}{m_O m_A}}\right], \tag{48}$$

which defines the quantity $\theta(C_O, C_A)$. With these expressions, the diffusion equations (46) take their final form:

$$\begin{cases} \dfrac{\partial C_O}{\partial t} = D_O^0 \dfrac{\partial^2 C_O}{\partial x^2} - m_O\,\tau^{-1}\,\theta(C_O, C_A) \\ \dfrac{\partial C_A}{\partial t} = D_A^0 \dfrac{\partial^2 C_A}{\partial x^2} - m_A\,\tau^{-1}\,\theta(C_O, C_A). \end{cases} \tag{49}$$

The terms proportional to $\theta(C_O, C_A)$ in (49) couple the equations in a nonlinear way, but their presence in these equations does not alter the basic mathematical character of the system which remains quasilinear (linear in the highest-order derivatives), of parabolic type. This implies, among other things, that in spite of the coupling, the *two* equations require *two*, not just one, boundary conditions at each point of the boundary; so that in a 1D problem, prescribing both conditions $C_O = C_O^{\text{surf}}$ *and* $\partial C_A/\partial x = 0$ (zero flux of A) at $x = 0$ will not raise any particular issue, in contrast to what was observed in Subsection 4.6 for the model based on the assumption of instantaneous local thermodynamic equilibrium.

5.4 A numerical example

We consider the same problem as in Subsection 4.6 of internal oxidation for the system O/Mn/MnO in a Fe matrix, but with two differences. First, we account for neither the effect of possibly large fractions of the P phase, nor the reduction of diffusion coefficients by oxides acting as obstacles. Second, the hypothesis of instantaneous local thermodynamic equilibrium is replaced by the simple kinetic equation (43) for the fraction of oxides. Under such conditions the equations of the problem reduce to the nonlinear diffusion equations (49), which are solved through some finite-difference-based spatial and temporal discretization, with an explicit scheme in time.

Equations (49), in their discretized form, are written at all internal nodes. At the surface node, however, there is no need to write equation $(49)_1$ for oxygen, since the concentration C_O is prescribed there; but it is necessary to write equation $(49)_2$ for manganese, since the condition of zero flux employed does not provide the value of $C_A \equiv C_{Mn}$. This requires a slight modification of this equation, because the terms in which the problem of local thermodynamic equilibrium is posed are a bit different on the surface, owing to the condition of prescribed concentration of O; see Appendix A for details.

Calculations are performed for fixed values of C_O^{surf} and C_{Mn}^{core}, 0.1 ppm and 4000 ppm respectively, and various values of the characteristic time τ of the precipitation of oxides: 0.1, 1, 5, 10, 20, 50 and 100 s. (These values are not chosen for their physical realism, but for the sole sake of qualitatively illustrating the influence of precipitation kinetics - of the Johnson-Mehl-Avrami type - upon internal oxidation). In addition we also display "reference results" corresponding on the one hand to complete absence of precipitation of oxides (with a very large value of τ of 10^6 s), and on the other hand to instantaneous local thermodynamic equilibrium (with a very small value, $\tau = 10^{-6}$ s).

Figure 7 first shows the distribution of the mass concentration of oxygen at time $t = 100$ s. For the value $\tau = 0.1$ s, local thermodynamic equilibrium is almost achieved everywhere at such an instant; the influence of precipitation kinetics upon the oxygen profile is then minor. When the characteristic time τ gradually increases, precipitation is more and more delayed, which leaves more and more time for oxygen to penetrate into the sheet before it is "pumped" by the chemical reaction; which is why its profile moves upwards.

Figure 8 similarly shows the distribution of the mass concentration of manganese at the same instant; Figure 8(a) offers a general view and Figure 8(b) a zoom near the surface.

One observes in Figure 8(a) that for $\tau = 100$ and 50 s, precipitation of oxides is so slow that

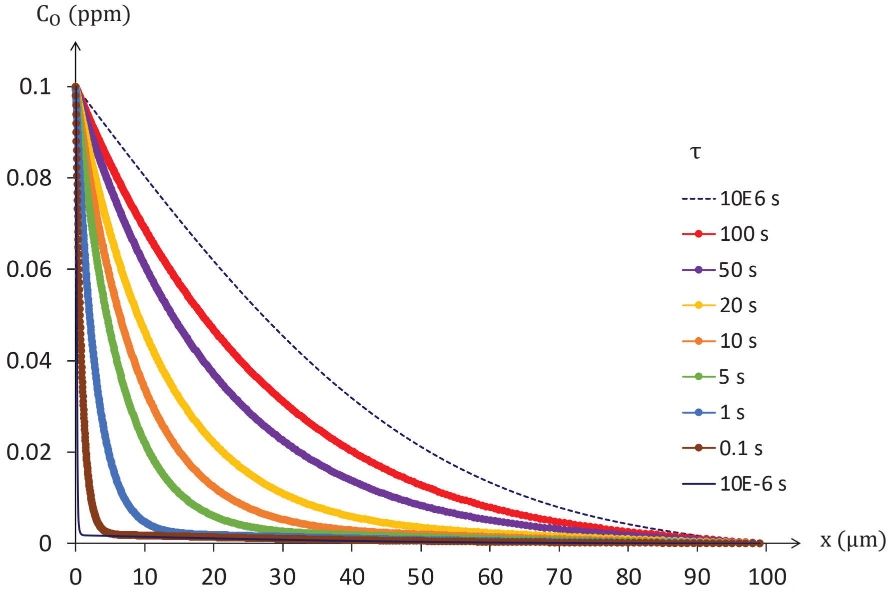


Fig. 7. Mass concentration of O at $t = 100\,\mathrm{s}$, for various values of the characteristic precipitation time τ - $C_O^{\mathrm{surf}} = 0.1\,\mathrm{ppm}$, $C_{Mn}^{\mathrm{core}} = 4000\,\mathrm{ppm}$.

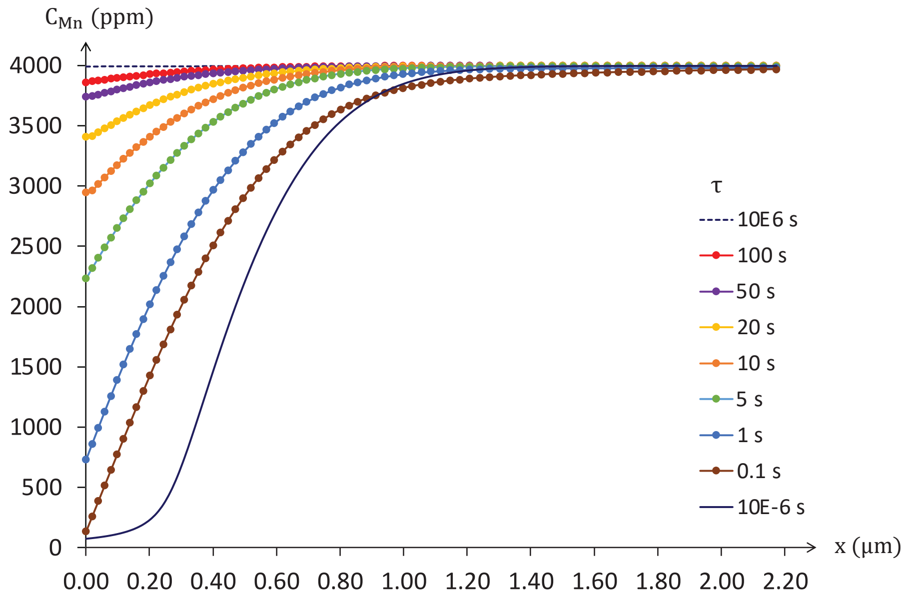
its impact upon the concentration of manganese is small; one just notes a slight decrease of C_{Mn} from the core value near the surface. When τ gradually decreases, however, this impact become more and more important and the concentration of manganese decreases more and more near the surface, due to pumping by the chemical reaction. For the smallest value of τ, 0.1 s, the manganese profile differs modestly from that obtained with the hypothesis of instantaneous local thermodynamic equilibrium.

Figure 8(b) permits to investigate the issue of zero or nonzero flux of manganese at the surface. From a purely theoretical point of view, the following remarks are in order:

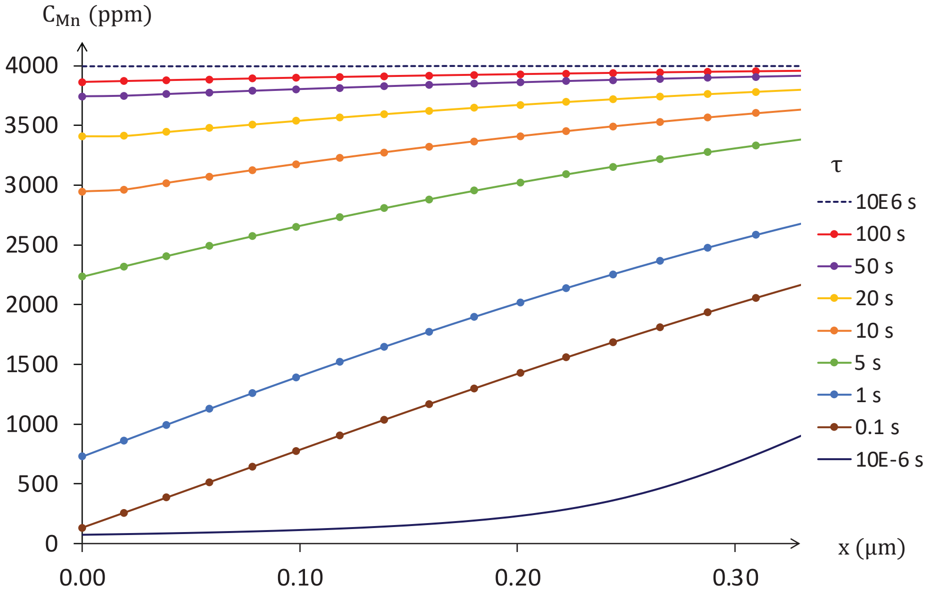
- In the presence of some precipitation kinetics, whatever the value of τ, even very small, the flux of manganese and therefore the derivative $\partial C_{Mn}/\partial x$ must be zero on the surface since this is imposed by the boundary conditions adopted.
- However, if local thermodynamic equilibrium is strictly respected, that is in the theoretical limit $\tau \to 0^+$, neither this flux nor this derivative can be zero there, as explained in Subsection 4.6.
- Compatibility of these two features demands that the region where $|\partial C_{Mn}/\partial x|$ is small decrease more and more in size as τ decreases down to zero: for small values of τ, this region must become a “boundary layer” of small thickness, analogous to those encountered in fluid mechanics, when a viscous fluid of very low viscosity flows past some immobile obstacle.

However computed results exhibit somewhat more complex features, for reasons connected to the numerical scheme:

- For the largest values of τ, 100, 50, 20 and 10 s, the initial slope (between the first two discretization points) of the curve $[C_{Mn}$ vs. $x]$ is almost nil, as expected.
- For smaller values of τ, 5, 1 and 0.1 s, this initial slope is no longer zero as theoretically predicted. This is because with a *fixed* mesh as employed here, it is impossible to



(a) General view



(b) Zoom near the surface

Fig. 8. Mass concentration of Mn at $t = 100\,\mathrm{s}$, for various values of the characteristic precipitation time τ - $C_O^{\mathrm{surf}} = 0.1\,\mathrm{ppm}$, $C_{Mn}^{\mathrm{core}} = 4000\,\mathrm{ppm}$.

reproduce the expected boundary layer of vanishingly small thickness in the limit $\tau \to 0^+$.

- Finally for $\tau = 10^{-6}\,\mathrm{s}$ (quasi-instantaneous local thermodynamic equilibrium), the initial slope, although strictly nonzero, is quite small. This is because pumping of manganese by precipitation is then efficient enough for this element to be notably depleted near the surface at time $t = 100\,\mathrm{s}$, which minimizes its output flux.

6 Concluding summary and perspectives

Some recent works (Leblond, 2011; Leblond *et al.*, 2013) opened the way to the *ab initio* prediction of the transition from internal to external oxidation, using Wagner (1959)'s classical analysis of internal oxidation extended through incorporation of the barrier effect of oxides upon diffusion. Unfortunately these works suffered from inevitable shortcomings tied to the strong hypotheses made by Wagner (1959). The aim of the present paper was to extend the analyses of Leblond (2011); Leblond *et al.* (2013) by removing some of Wagner (1959)'s most severely restrictive assumptions, so as to broaden the range of situations in which a theoretical prediction of the transition is possible.

The first major restriction of Wagner (1959)'s analysis lied in use of a theoretical framework limited in essence to small values of the fraction of oxides; this was in contradiction with the fact that the "critical" value of this fraction, above which internal oxidation is no longer possible, must obviously be comparable to, not much smaller than, unity. As a first step toward a solution of this issue, Section 2 presented an extended framework considering arbitrarily large values of the fraction of oxides, essentially inspired from that proposed by Brunac *et al.* (2010) but containing somewhat different diffusion equations, for reasons which were analyzed.

Section 3 then presented an extension of Leblond (2011); Leblond *et al.* (2013)'s analyses of the transition from internal to external oxidation, based on the more general model just expounded. The output was a smaller value of the predicted critical fraction of oxides governing the transition, as compared to that in the work of Leblond (2011). This smaller value was found to better agree with the old, but still unchallenged experimental observation of Rapp (1961) for the $O/In/In_2O_3$ system in an Ag matrix.

Another severe restriction of Wagner (1959)'s work was consideration of an oxide with an extremely low solubility product, prohibiting coexistence of oxygen and the oxidizable element in their dissolved forms in the matrix. Section 4 tackled this other issue by modifying the preceding analysis through introduction of a finite, nonzero solubility product. The treatment, which extended that of Huin *et al.* (2005) of a simpler version of the problem, resulted in coupled nonlinear ordinary differential equations on two variables, too complex to be solvable analytically but well fit for a numerical solution. Numerical results evidenced existence or absence of a brutal transition from internal to external oxidation, depending on the parameters of the system.

In spite of the interest of these results, they raised several issues which appeared to be basically tied to the inadequacy of the hypothesis of instantaneous local thermodynamic equilibrium near the surface of the plate, due to quickness of the processes occurring there. The object of the final Section 5 was to propose a tentative solution to these difficulties, in the form of modified equations of diffusion/precipitation incorporating some kinetic equation for the precipitation of oxides, depicting relaxation toward the local state of thermodynamic equilibrium. Introduction of such an equation was shown to indeed settle the important issue of impossibility, when instantaneous local thermodynamic equilibrium is assumed, of prescribing a boundary condition for the oxidizable element independent of that for oxygen.

However, the analysis of Section 5 was essentially qualitative, being based on overly simplified assumptions, plus an elementary kinetic model making no claim to a detailed description of underlying mechanisms. Since this preliminary analysis has revealed that introduction of kinetics of precipitation of oxides is a keypoint in the theoretical description of internal oxidation, and especially of the transition to external oxidation, the next step will be to develop extended equations of diffusion/precipitation incorporating realistic, necessarily complex kinetic models, accounting in detail for nucleation and growth of individual oxides.

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Data availability

The raw/processed data required to reproduce these findings cannot be shared at this time due to technical or time limitations.

References

Brunac J.B., Huin D., Leblond J.B. (2010). Numerical implementation and application of an extended model for diffusion and precipitation of chemical elements in metallic matrices, *Oxid. Metals*, **73**, 565-589.

Christ H.J., Christl W., Sockel H.G. (1986). Carburization of high-temperature materials. I. Mathematical model description of the penetration and simultaneous precipitation of a compound of the diffusing element, *Werkst. Korros.*, **37**, 385-390 (in German with English title).

Douglass D.L. (1995). A critique of internal oxidation in alloys during the post-Wagner era, *Oxid. Metals*, **44**, 81-111.

Fortunier R., Leblond J.B., Pont D. (1995). Recent advances in the numerical simulation of simultaneous diffusion and precipitation of chemical elements in steels, in: *Phase Transformations During the Thermal/Mechanical Processing of Steel*, Hawbolt and Yue, eds., the Canadian Institute of Mining, Metallurgy and Petroleum, Montreal, Canada, pp. 357-371.

Gesmundo F., Castello P., Viani F., Roos C. (1998). The effect of supersaturation on the internal oxidation of binary alloys, *Oxid. Metals*, **49**, 237-260.

Gesmundo F., Gleeson B. (1995). Oxidation of multicomponent two-phase alloys, *Oxid. Metals*, **44**, 211-237.

Gesmundo F., Niu Y. (1999). The formation of two layers in the internal oxidation of binary alloys by two oxidants in the absence of external scales, *Oxid. Metals*, **51**, 129-158.

Gesmundo F., Viani F., Niu Y. (1996). The internal oxidation of two-phase binary alloys under low oxidant pressure, *Oxid. Metals*, **45**, 51-76.

Gesmundo F., Viani F., Niu Y. (1997). The internal oxidation of two-phase binary alloys beneath an external scale of the less-stable oxide, *Oxid. Metals*, **47**, 355-380.

Huin D., Flauder P., Leblond J.B. (2005). Numerical simulation of internal oxidation of steels during annealing treatments, *Oxid. Metals*, **64**, 131-167.

Huin D., Lanteri V., Loison D., Autesserre P., Gaye H. (1996). Modelling of internal oxidation of several elements, in: *Microscopy of Oxidation - 3*, Newcomb and Little, eds., the Institute of Metals, London, pp. 573-586.

Kirkaldy J.S. (1969). On the theory of internal oxidation and sulphation of alloys, *Can. Metall. Quart.*, **8**, 35-38.

Laflamme G., Morral J.E. (1978). Limiting cases of subscale formation, *Acta Metall.*, **26**, 1791-1794.

Leblond J.B. (2005). Mathematical results for a model of diffusion and precipitation of chemical elements in solid matrices, *Nonlinear Anal. B: Real World Applic.*, **6**, 297-322.

Leblond J.B. (2011). A note on a nonlinear variant of Wagner's model of internal oxidation, *Oxid. Metals*, **75**, 93-101.

Leblond J.B., Bergheau J.M., Lacroix R., Huin D. (2017). Implementation and application of some nonlinear models of diffusion/reaction in solids, *Fin. Elem. Anal. Des.*, **132**, 8-26.

Leblond J.B., Pignol M., Huin D. (2013). Predicting the transition from internal to external oxidation of alloys using an extended Wagner model, *C.R. Mecanique*, **341**, 314-322.

Niu Y., Gesmundo F. (2001). An approximate analysis of the external oxidation of ternary alloys forming insoluble oxides. I: High oxidant pressures, *Oxid. Metals*, **56**, 517-536.

Ohriner E.K., Morral J.E. (1979). Precipitate distribution in subscales, *Scripta Metall.*, **13**, 7-10.

Oikawa H. (1982). Lattice diffusion in iron - A review, *Trans. Iron Steel Inst. Japan*, **68**, 1489-1497.

Rapp R. (1961). The transition from internal to external oxidation and the formation of interruption bands in silver-indium alloys, *Acta Metall.*, **9**, 730-741.

Rapp R. (1965). Kinetics, microstructures and mechanism of internal oxidation - Its effect and prevention in high temperature alloy oxidation, *Corros.*, **21**, 382-401.

Stott F.H., Wood G.C. (1988). Internal oxidation, *Mater. Sc. Technol.*, **4**, 1072-1078.

Thermodata (2005). Electronic data bank for thermodynamic quantities, available online at the address http://thermodata.online.fr.

Wagner C. (1959). Reaktionstypen bei der oxydation von Legierungen, *Zeitschrift Elektrochemie*, **63**, 772-782 (in German).

Whittle D.P., Gesmundo F., Bastow B.D., Wood G.C. (1981). The formation of solid solution oxides during internal oxidation, *Oxid. Metals*, **16**, 159-174.

Zhao W., Kang Y., Orozco J.M.A., Gleeson B. (2015). Quantitative approach for determining the critical volume fraction for the transition from internal to external oxidation, *Oxid. Metals*, **83**, 187-201.

A Appendix: diffusion equation of the oxidizable element on the surface in the presence of precipitation kinetics

Let us first examine the problem of local thermodynamic equilibrium on the surface, where C_O is prescribed. Equations (44), which were used in Subsection 5.3 to solve this problem, are applicable in the interior of the domain considered, but not on its surface. Indeed the first two equations correspond to the mass balance of O and A in the state of thermodynamic equilibrium, for *given values of the total fractions* F_O, F_A, that is for a fixed chemical composition; but the quantity known on the surface is *not*, for oxygen, its total fraction F_O but its matrix concentration C_O which is prescribed.

It is reasonable to assume that on the surface, the state of thermodynamic equilibrium which is referred to in the kinetic equation (43), is that for which the equilibrium concentration C_O^{eq} is precisely that prescribed on the surface, C_O^{surf}. (In contrast for the oxidizable element A, the concentration of which is not prescribed, it is natural to as usual identify the total fraction F_A as the given data). Under such conditions the equations defining the problem of local thermodynamic equilibrium read, instead of (44):

$$\begin{cases} C_O^{\mathrm{eq}} & = C_O^{\mathrm{surf}} \\ F_A & = C_A^{\mathrm{eq}} + \frac{m_A}{M_P} P^{\mathrm{eq}} \\ C_O^{\mathrm{eq}} C_A^{\mathrm{eq}} & = K. \end{cases} \tag{A.1}$$

Now combination of equations $(41)_2$ and $(\mathrm{A}.1)_2$ yields

$$P^{\mathrm{eq}} - P = \frac{M_P}{m_A}\,(C_A - C_A^{\mathrm{eq}})$$

which is identical to equation (45) of the text, but for element A only. It immediately follows that the diffusion equation $(46)_2$ for A still holds. This equation may be put into the form

$$\frac{\partial C_A}{\partial t} = D_A^0 \frac{\partial^2 C_A}{\partial x^2} - m_A\,\tau^{-1}\,\theta(C_O^{\mathrm{surf}}, C_A) \tag{A.2}$$

which is analogous to equation $(49)_2$, but the expression of the function $\theta(C_O^{\mathrm{surf}}, C_A)$ now differs from that provided by equation (48) and is simpler:

$$\theta(C_O^{\mathrm{surf}}, C_A) \equiv \frac{1}{m_A}\,(C_A - C_A^{\mathrm{eq}}) = \frac{1}{m_A}\left(C_A - \frac{K}{C_O^{\mathrm{surf}}}\right) \tag{A.3}$$

where equations $(\mathrm{A}.1)_{1,3}$ have been used.

A final remark pertains to the condition of zero flux of element A on the surface, which does not clearly appear in the theoretical diffusion equation (A.2). This condition is to be accounted for when defining the discretized equivalent of the quantity $D_A^0 \frac{\partial^2 C_A}{\partial x^2}$.