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Numerical Model for Oxide Scale Growth with Explicit Treatment of Vacancy Fluxes

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Abstract. In the framework of research on behaviour of nuclear waste containers, to evaluate the effects of possible evolution of experimental conditions, as well as evolution of parameters controlling oxidation rate during long-term interim storage, a numerical model has been developed in order to take into account non-stationary states. To anticipate effects like cold working of the metal on the scale growth kinetics and risks of scale detachment by over saturation of vacancies at the metal/oxide interface in the course of scale growth, the model is based on the calculation of chemical species, but also vacancies profiles evolution in the oxide and the metal following a simple time integration. An original numerical treatment is proposed to easily describe elimination of vacancies by introducing sink strength in the metal. The first calculations are presented and discussed.

Introduction

Context. For high-level nuclear waste containers in long-term interim storage, dry oxidation will be the first and the main degradation mode. The reason is that, for this kind of waste, the temperature on the surface of the containers will be high enough to avoid any condensation phenomena for several years. Even if the scale growth kinetics is expected to be very slow since the temperature will be moderate at the beginning of the storage (around 300°C) and will keep on decreasing, the metal thickness lost by dry oxidation over such a long period must be evaluated with a good reliability. To achieve this goal, modeling of the oxide scale growth is necessary and this is the aim of the dry oxidation studies, performed in the frame of the COCON programme [1].

All existing oxidation models are based on the two main oxidation theories developed by Wagner [2] between the 1930s and 1970s on the one hand, and by Cabrera and Mott [3] in the 1960 and next by Fromhold [4] on the other hand. These used to be associated with high temperature behaviour for Wagner's theory and with low temperature for the second. Indeed it is certainly more relevant to consider their range of application in terms of the oxide scale thickness rather than in terms of temperature. In the case of dry oxidation of waste containers, which theory should an appropriate model rely on? It can be expected that the oxide scale could have a thickness ranging from a few tens of nanometers up to several tens of micrometers depending on temperature and class of alloys chosen. At the present time, low-alloyed steels or carbon steels are considered candidate materials for high nuclear waste package containers in long term interim storage as they will undergo general corrosion during the second stage of atmospheric corrosion rather than localized corrosion which is much more complicated to anticipate over a long time period. For this type of alloys, the scale formed during the dry oxidation stage will be "rapidly" thick enough to neglect the Mott field. Hence, in a first step, some basic models based on a parabolic rate assumption have been derived from experimental data on iron and on low-alloy steel oxidations. Their extrapolation to long oxidation periods confirms that the expected damage due to dry oxidation could be small (less than 100µm for a 100 year period) [5]. However, the reliability of this kind of model is poor, since it is based on the assumption that a single elementary process,

volume diffusion phenomena in the scale, controls the oxidation rate during the whole storage period which furthermore is not always in accordance with the kinetics measurements over long duration [5]. The reason is that in reality, several other phenomena play a major role in the oxidation rate at this temperature. The lower the temperature, the more diffusion along grain boundaries should become the major transport mechanism. Then, grain size distribution evolution in the oxide should be taken into account. Second, it is well known that whether the metal is cold-worked or not can significantly affect oxidation mechanisms and kinetics. Indeed, a larger number of dislocations leads to a higher vacancy annihilation capability. As a consequence, the decrease in the number of defect not only lowers the diffusion rate in the metal but also leads to a reduced tendency for vacancies to accumulate and cause local scale detachment. In their study for Yucca Mountain site [6], Larose and Rapp outline the importance of these latter phenomena. In addition, experimental results on the low-alloy steel [7] show that even if alloying elements could not be found in the oxide scale, their distribution in the alloy near the metal/oxide interface certainly would affect the diffusion transport of oxidized species in the metal and hence modify the scaling rate.

We then propose to build a non-steady state numerical model able to reproduce all the major mechanisms described above in order to have a more reliable tool to describe the oxidation kinetics over long periods of time.

Modelling oxidation. Wagner's theory links oxidation kinetics and concentration profiles in the oxide and in the metal to vacancies concentration and diffusion coefficient. In the 70ies, Smeltzer et al. [8] and Bastow et al [9] have realized numerical resolutions of Wagner's model by finite differences algorithm for pseudo-stationary state. Since these first models which take into account only a volume diffusion mechanism, various models challenge to connect microstructure and oxidation rate, considering processes like the effect of stress on diffusion [10], grain boundary diffusion [11].... However, they always presume that a pseudo-steady state is reached. To build a model able to anticipate effects like changes in experimental conditions (temperature, atmosphere), evolution of parameters controlling transport in the scale (evolution of microstructure for example), changes at interface (thermodynamics equilibrium evolution) or in the metal, pseudo-steady state assumption cannot be maintained and evolution of both oxide and substrate have to be considered. Nesbitt [12] has created a numerical model using finite differences algorithm to simulate multi-component diffusion induced by high temperature oxidation, including the effect of phase dissolution in the substrate, nevertheless the defects profiles are not explicitly calculated. In a recent study [13], Nidjam et al. also present an interesting model for thermal oxidation of ternary alloys for a non-simple parabolic kinetics. However the presumed shape of the scale growth kinetics is an input data of the model from which compositional changes in the oxide phase are calculated, but not an output result. Alternatively, Monceau et al.[14] have performed non-steady state calculations for kinetic demixing profile in oxide solid solution under potential chemical gradient, taking for granted defects but only the oxide scale. So, as we will see later, the first stage of the construction of our model has been to compute the Wagner's model without the pseudo-steady state hypothesis and with explicit calculations of vacancy profiles, as well as considering both the substrate and the oxide. It requires taking care of the relative motion of the substrate crystal lattice watched by oxide crystal lattice (or reverse case) which is directly linked to the elimination of vacancies at the interface.

About elimination of vacancies. For a cationic transport mechanism, in every model derived from Wagner's one, all the vacancies are supposed to be annihilated at the interface. Hence, the interface motion taking the metal lattice as referential is straightforwardly deduced from the quantity of metal recession due to oxide growth, and as a result it is proportional to the parabolic kinetics growth. On the other hand, as revealed by evidence of voids formation encountered from time to time, vacancies are not always all annihilated at the interface. Gesmundo and Hou have proposed theoretical analysis of voids formation kinetics at the alloy/oxide interface, taking into account vacancy flux from the Kirkendall effect in the alloy and vacancy flux due to oxide growth [15]. His model assumes immobile interfaces and that all the vacancies reaching the interface condensate to

form voids. Indeed it would surely be, in most cases, more appropriate to consider that vacancies are neither all eliminated at interface nor all injected in the metal, but rather partially annihilated at the interface and hence partially injected. Pierraggi et al. [16] have linked the capacity of interfaces to annihilate incoming vacancies to the ability for interface dislocations to climb. In case of pure cationic growing scales, they showed that cationic vacancies could only be annihilated by climbs of misorientation or misfit dislocations in the metal, these latter being energetically favoured. On the basis of this work, some first non stationary-state calculations on vacancies profiles in the oxide have been done by Monceau (see in [17]) considering a constant rate k_l of annihilation of vacancies at the interface metal/oxide. As a consequence, the shape of the growth kinetics is described by $de/dt=1/(1/k_l+2e/k_p)$ where e is the oxide thickness and t the time. Only few studies have focused on the “future” of vacancies injected in the metal despite studies dealing with voids formation. Caplan et al. [18] and Carpenter and Ray [19] showed that oxide/metal contact was better on cold worked samples than on annealed ones. They agree to conclude that cold worked iron absorbed better vacancies. Inspired by Francis and Lees [20] who prove the evidence of injecting vacancies in the metal during iron scale growth by cationic transport, recent attractive experiments attempt to demonstrate that injected vacancies in the metal can migrate upon large distances without condensating in volume [21]. Indeed, as for the elimination of vacancies at the interface, vacancies in the alloy are also to some extent annihilated (but also created) in the alloy bulk. Actually when diffusion proceeds in a crystal via point defects which create or eliminate at discrete sinks such as dislocations distribution in the bulk, the defects can neither be considered as conservative (zero sink strength) nor as being at local equilibrium (infinite sink strength). However these two drastic and opposed assumptions are often taken for granted in classical treatment of diffusion phenomena. Indeed, Martin and al. [22] have established that the effect of finite sink strength is to modify the Fick’s law to a first order in inverse sink strength for larger sink strength. A complete treatment (including lower sink strength) has been done via numerical modelling by Desgranges and applied in the case interdiffusion experiments exhibiting a strong Kirkendall effect [23]. The results show that sink activity has a definite influence on the shape of interdiffusion profile. First, a part of this model has inspired the numerical treatment used to correctly and easily describe elimination of vacancies at the interface and thus relative motion between the substrate lattice and the oxide lattice in the oxidation model proposed below. And, second, elimination/creation of vacancies in the bulk substrate will be computed following the same treatment as in [22-23].

The aim of the presented model is to build a numerical code able to reproduce all the major mechanisms described above in order to have a more powerful tool to describe the oxidation rate over long periods. This model is currently under development. We mainly present here the general description and the way we manage to solve the set of equations numerically, and only a few preliminary results.

General description of the model

The “1D” system under consideration can be described as a “sandwich-like” schematic image (Fig. 1) composed of a semi-infinite metal, the metal/scale interface, the oxide scale, the oxide/gas interface and a semi-infinite layer of gas.

In each layer we define the different species concentrations. The chemical species are the metallic species (A, B ,...), and an oxidant species X. An overview of the different steps that we wish to deal with in the final model is as follows:

- i) the transport of chemical species by atomic diffusion via point defects but also by diffusion along short-circuits like grain boundaries or porosity in the oxide scale ;
- ii) the interface movement considered either as an interface reaction taking place under conditions of a local equilibrium, or, by introducing a step reaction rate, that is, whether the oxidation reaction is considered to be instantaneous or not with respect to the diffusion.
- iii) the annihilation or creation of point defects at interface and in the metal volume;

iv) the electronic fluxes, effect of high field on migration, and electron tunnelling. However in a first stage, these phenomena which will be rate determining steps for thin oxide scales will not be introduced. This has been done in work by Martin and Fromm [24-25].

At the present stage of development, explicit diffusion of vacancies, moving interfaces, explicit creation, annihilation or injection of vacancies, anionic, cationic and mix transport mechanisms have been introduced and non-stationary states are treated by a numerical calculation of time evolution of the system.

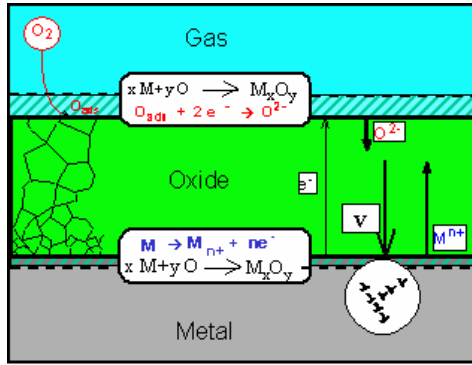


Fig. 1. Schematic representation of mechanisms involved in the scaling rate

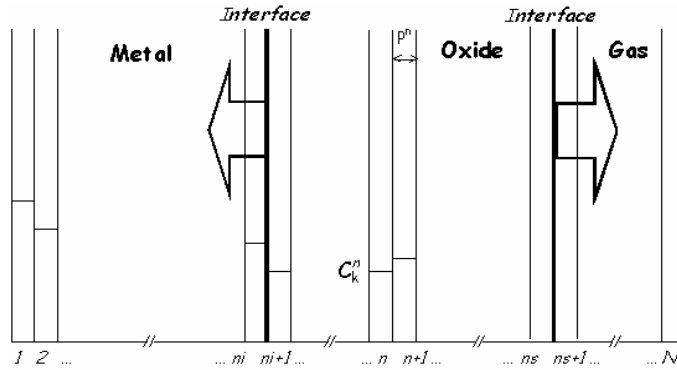


Fig. 2. Schematic representation of the concentration profile

Set of equations governing the evolution of the concentration profiles. To calculate the time evolution of the system, we consider the profile evolution of the different species. To consider diffusion with non-conservative defects, we use Martin's description (see [22]). Hence, as shown in Fig. 2, concentration profiles are described by N labelling slabs of contiguous lattice planes with a thickness p_n .

We define in each slab n the concentration of the different species $C_k^n = \frac{N_k^n}{N_{sites}}$.

Following Fick's first law, using reduced units, the flux of chemical species i passing from slab n to $n+1$ is given in the referential corresponding to the nature of the considered slab by:

$$J_i^{n \rightarrow n+1} = - \sum_k d_{ik} \frac{C_k^{n+1} - C_k^n}{\frac{1}{2}(p^n + p^{n+1})} \quad (1)$$

with $d_{ik} = - \sum_j \frac{M_{ij}}{kT} \frac{\partial(\mu_i - \mu_v)}{\partial C_k}$ and $M_{ij} = \delta_{ij} z v_i C_v C_i \text{Exp}(-Q/kT)$ (2a and 2b)

Note that the diffusion coefficient varies with respect to vacancies concentrations in the slab. In the oxide, we distinguish two types of vacancies, anionic and cationic and two sub-lattices for the exchange mechanism. Hence, the vacancy fluxes in the oxide in the oxide lattice referential are nothing else but :

$$J_{V_o}^{n \rightarrow n+1} = - J_O^{n \rightarrow n+1} \text{ for anionic vacancies} \quad (3a)$$

$$J_{V_M}^{n \rightarrow n+1} = - \sum_{k=A,B,\dots} J_k^{n \rightarrow n+1} \text{ for cationic vacancies} \quad (3b)$$

Following [22-23], assuming that the vacancy creation or annihilation in a metal slab n only increases or decreases the number of planes in the latter slab (without affecting cross section) the conservation equations now show:

$$\dot{C}_i^n = \frac{\partial C_i^n}{\partial t} = - \frac{J_i^{n \rightarrow n+1} - J_i^{n-1 \rightarrow n}}{p^n} - C_i^n \frac{\dot{p}^n}{p^n} \text{ with } \frac{\dot{p}^n}{p^n} = \frac{\partial C_v}{\partial t} \Big|_{sinks} \quad (4a \text{ et } 4b)$$

In Eq. 4a, the second term of the Right Hand Side (RHS) accounts for the change in the site concentration of species i resulting from the change in the number of sites in slab n keeping the atom fraction constant. This term disappeared for slabs in the oxide.

In the slab ni , the RHS of Eq.4b is null if all the vacancies are supposed to be injected in the metal, and equal to the metal flux injected in the oxide if all the vacancies are supposed to be annihilated at the interface.

In the metal, creation or annihilation of vacancies in volume can be simply added, assuming that vacancy source and sink are formed by a uniform dislocation density ρ the local rate of change in vacancy composition is given by :

$$\left. \frac{\partial C_v}{\partial t} \right|_{sinks} = -\rho d_{vv} (C_v^{eq} - C_v) \quad (5)$$

To compute time evolution we used a classical explicit finite difference algorithm with a small time increment Δt given by the stability criterion: $d_{max} \Delta t < 1/4 \Delta x^2$

Algorithm for moving boundaries. To authorize growth of the scale by cationic and anionic transport we define two moving boundaries: between the slab ni and $ni + 1$ for the interface metal/oxide and between ns and $ns+1$ for the oxide/gas interface. For each time step the thickness p_{ni} (p_{ns}) and p_{ni+1} (p_{ns+1}) as well as concentrations of the corresponding slabs are recalculated in order to achieve local equilibrium over the two slabs around the interface. The complete algorithm is described in [23] and allows the movement of the interface in the entire system by incrementing variable ni (and ns) which marks the interface position when one of the slab becomes too large. For example, equilibrium can be simply defined by fixed equilibrium concentrations ($^{eq}C^{oxide}$; $^{eq}C^{metal}$) as in a binary phase diagram. In this case, the interface which position is always simply calculated by Eq. 6, obeys the classical rate equation Eq.7 :

$$\xi = \sum_{n=1}^{ni} p^n \quad (6)$$

$$\dot{\xi} = \frac{\partial \xi}{\partial t} = \frac{J^{ni-1 \rightarrow ni} - J^{ni+1 \rightarrow ni+2}}{C^{oxide} - C^{metal}} \quad (7)$$

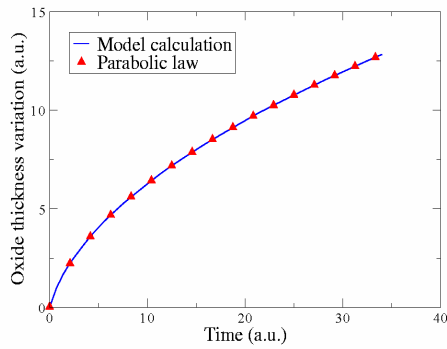
The algorithm for interface motion can also be used for a more complex equilibrium phase diagram. For a multicomponent system, minimisation of the free energy over the two slabs around the interface gives the proportion for each phase from which the thickness p_{ni} (p_{ns}) and p_{ni+1} (p_{ns+1}) are deduced, hence changing the interface position following Eq.6.

Preliminary results

As the first step of this work, the model has been used considering vacancies as conservative species in the metal ($\rho=0$; the second term of the RHS in the equation Eq. 5 is null). For initial conditions, we define the concentration of each species in order to describe the system: for slabs 1 to ni , (i.e. the metal layer) the oxygen concentration is null, for slabs $ni+1$ to ns (the oxide layer), the concentrations of all the species is non-null, and finally, for slabs $ns+1$ to N (the gas layer), the concentrations of oxygen vacancies is null.

For boundary conditions, we chose fixed equilibrium vacancy concentrations at the interfaces. Notice that at the surface, the concentrations of the equilibrium vacancies in the oxide can be directly related to a fixed oxygen partial pressure [26]. Last, we have applied the two severe cases for behaviour of cationic incoming vacancies at the interface : in the first case vacancies are all eliminated at the interface, in the second case, all incoming vacancies are injected in the metal (RHS of Eq. 4b is taking null even for slab ni). With the set of parameters described above, the model has been numerically solved using $N=100$ or 300 slabs.

Calculations with elimination of all vacancies at the interface. Kinetics parameters (d_{ik}) have been chosen to reproduce an oxide scale with a pure cationic growth. Fig. 3a shows the calculated evolution of the oxide thickness. As expected from the chosen initial conditions, the scaling rate is parabolic. Fig. 3b shows the evolution of metallic vacancies profile. In this case, the motion of the interface metal/oxide is only a result of metal recession due to vacancies elimination, given that no inward diffusion is possible with the chosen parameters. In this first calculation, the metal lattice volume has been arbitrary chosen equal to the oxide lattice volume. Hence the oxide growth at the surface by cationic transport mechanism being equal to the metal recession due to elimination of vacancies, in the metal lattice referential the surface seems to be immobile. The same calculation, considering the oxide expansion with an oxide lattice volume twice the metal lattice volume, would have lead to an apparent motion of the surface in the metal lattice referential despite the elimination of all incoming vacancies at the interface (Fig. 3c).

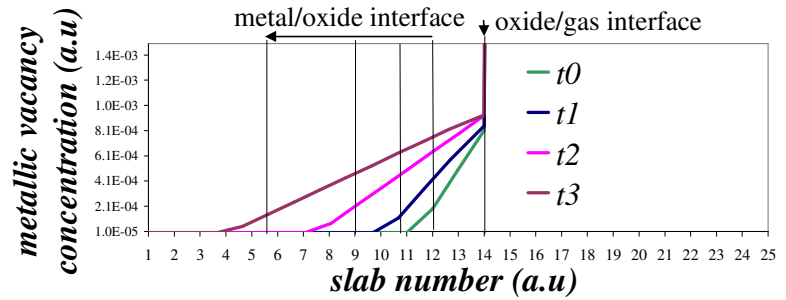


a)

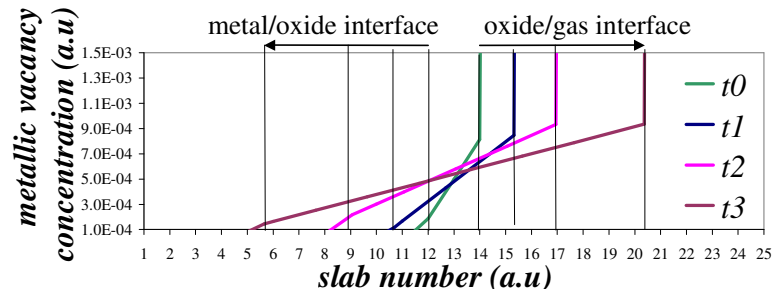
Fig. 3. model for pure cationic transport mechanism and elimination of all incoming vacancies at the interface

a) Evolution of the oxide thickness with time

b) and c) Evolution of metallic vacancies profiles in the metal referential.



b) $\Omega_{\text{oxide}} = \Omega_{\text{metal}}$



c) $\Omega_{\text{oxide}} = 2 \Omega_{\text{metal}}$

Calculations with mixed anionic-cationic growth and injection of all the cationic vacancies in the metal. For this case, kinetic parameters (d_{ik}) have been chosen to reproduce an oxide scale with a slightly larger anionic mobility than cationic mobility. Also, the cationic vacancies are no longer annihilated at the metal/oxide interface, but all injected in the metal. Fig. 4a shows the associated evolution of profiles of metallic vacancies in the oxide during the first time steps. It shows that the concentration profile quickly develops into a linear gradient, which is the expected stationary profile in respect to the chosen equilibrium conditions at the interfaces. For long time simulation leading to large-scale growth, the concentration profiles of metallic vacancies in the oxide layer shown in Fig 4b stay linear since stationary state has been reached. We can also see on this Fig. that the growth of the oxide layer is slightly more important at the metal/oxide interface than at the oxide/gas interface, as expected from the chosen set of kinetics parameters. In fact in this case, with vacancies being all injected in the metal, the motion of the interface in the metal lattice referential is only attributable to the anionic growth mechanism, and the motion of the surface to the cationic growth mechanism because lattice volumes have been, in this calculation, artificially chosen to be equal in the metal and in the oxide. The shape of the vacancies concentration profile in the metal suggests that further growth of the oxide could lead to oversaturation of vacancies in the metal as a result of vacancies injection and therefore to voids formation, as no sink strength is present in the metal.

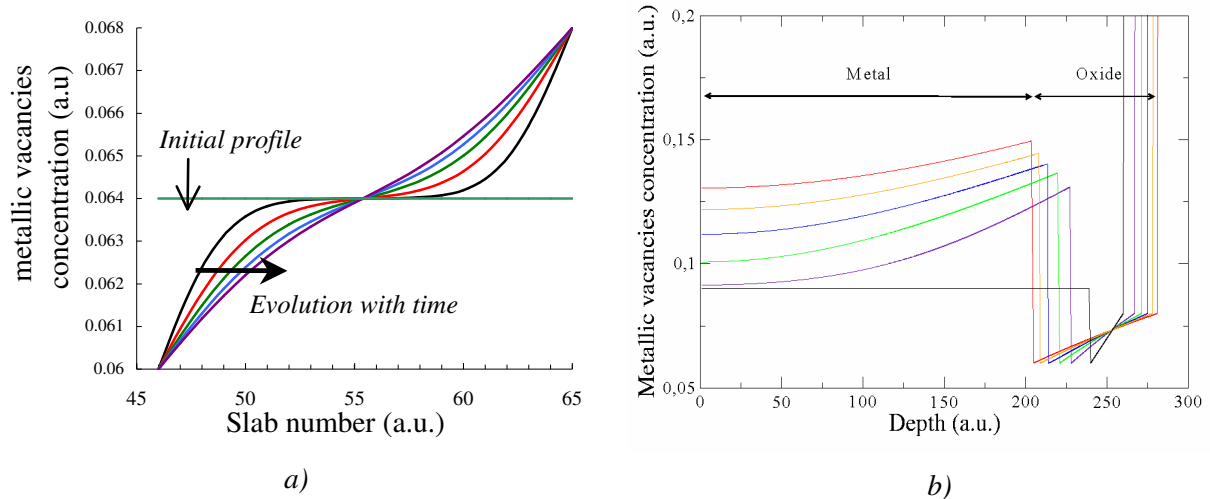


Fig. 4. Evolution of the metallic vacancies concentration a) in the oxide for the first time steps (transition stage) and b) for long time simulation in the metal and in the oxide (stationary profile in the oxide is reached)

Future development. The next step will be to use the model with a non-null density of dislocations to evaluate the influence of the non-conservation of vacancies on the metal oxidation rate. In a second phase, diffusion via short-circuits will be introduced by defining a density of shortcuts in each oxide slab, following a description similar to the one used to introduce a dislocation density in the metal.

Conclusion

A numerical model has been built to treat Wagner's model but without the pseudo-steady state hypothesis and with explicit calculations of vacancy profiles, as well as considering both the substrate and the oxide. Moreover, the case of mixed anionic-cationic transport mechanism can be considered. This model is developed in the framework of research on high level nuclear waste metallic containers behaviour during long term interim storage. Indeed for this specific system which will operate at an intermediate temperature range, the role of vacancies in the metal near the interface, the diffusion via short-circuits path in the oxide, as well as the evolution of system parameters with time, have to be handled. The model is based on an original numerical treatment to correctly and easily describe elimination of vacancies at the interface and thus relative motion between the substrate lattice and the oxide lattice, even for non-stationary states. It has been first applied in the borderline cases : considering that incoming vacancies at the interface are all eliminated or all injected in the metal. As expected from chosen boundary conditions, the calculated kinetics rate is parabolic in both cases. In a next step, intermediate case will be regarded and elimination/creation of vacancies in the bulk substrate will be computed following a similar treatment. Hence, the model should be able to quantify well known effects of cold working of metal on oxidation behaviour, but often not introduced in models.

Acknowledgment

Stimulating discussions with G. Martin (CEA) are gratefully acknowledged.

Notations

T : temperature

$V_O V_M$: oxygen (anionic) and metallic (cationic) vacancies

N_k^n : number of species k in slab n

C_k^n : concentration of species k in the slab n

${}^{eq}C^{oxide}$, ${}^{eq}C^{metal}$: equilibrium concentration respectively in the oxide, in metal

$d_{ik} = \frac{D_{ik}}{(\text{system length})^2}$: reduced coefficient of diffusion (D_{ik} : coefficient of diffusion)

p^n : reduced length of the slab n M_{ij} : mobility

v_i : attempt frequency ρ : dislocation site density

z : coordinence Q : activation energy

ξ : interface position μ_i : chemical potential of i species

$J_i^{n \rightarrow n+1}$: flux of the species i from the slab n to the slab $n+1$

$\dot{x} = \frac{\partial x}{\partial t}$: time derivative of x $\delta_{ij} = 1$ (for $i = j$) = 0 (for $i \neq j$) : Kronecker's symbol

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