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Model for Low Temperature Oxidation during Long Term Interim Storage

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For high-level nuclear waste containers in long-term interim storage, dry oxidation will be the first and the main degradation mode during about one century. The metal lost by dry oxidation over such a long period must be evaluated with a good reliability. To achieve this goal, modelling of the oxide scale growth is necessary and this is the aim of the dry oxidation studies performed in the frame of the COCON program. An advanced model based on the description of elementary mechanisms involved in scale growth at low temperatures, like partial interfacial control of the oxidation kinetics and/or grain boundary diffusion, is developed in order to increase the reliability of the long term extrapolations deduced from basic models developed from short time experiments. Since only few experimental data on dry oxidation are available in the temperature range of interest, experiments have also been performed to evaluate the relevant input parameters for models like grain size of oxide scale, considering iron as simplified material.

Keywords : Oxidation, Iron, Low-Temperature, Modelling, Vacancies.

Introduction

For high level nuclear waste containers in long term interim storage, dry oxidation will be one of the main degradation modes. The reason is that, for this kind of waste, the temperature at the surface of the containers will be high enough to avoid any condensation phenomena for several decades of years. To evaluate the metal thickness lost by dry oxidation over such a long period, modelling of the oxide scale growth is necessary and this is the aim of the dry oxidation studies, performed in the frame of the COCON (COrrosion of CONtainers) research program established by the CEA [1]. It is clear that long term prediction of the corrosion behaviour of metals and alloys needs the combined information from the various experimental and modelling approaches. Moreover it is essential to achieve an understanding of the processes that control the corrosion of container materials.

Only a few studies dealing with iron and steel oxidation in the temperature range concerned by containers in long term interim storage (between 100°C and 400°C) have been reported in the literature. Moreover, most of these studies are focused on the first stages of the film growth and are therefore performed under a very low oxygen partial pressure and for only few hours. To handle this lack of data, some oxidation tests under atmospheric pressure and at low temperature have been performed for several hundred hours. For this experimental study, iron has been considered as one of the model materials and has been studied at low temperature (below 500°C) and under dry air or air with 2 vol% H_2O which can be considered as the typical atmosphere of the interim storage site. For modelling, since a simple control by volume diffusion cannot accurately reproduce oxidation kinetics at low temperature, an advanced model is developed in order to include grain boundary diffusion and partial interfacial control of the oxidation kinetics. A step towards this aim is to build a model with

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explicit treatment of vacancy fluxes. The experimental study is first presented and second, our approach for modelling of oxide growth at low temperature.

1- Experimental Study : Low Temperature Oxidation of pure Iron

At any temperature below 570°C, at atmospheric pressure, only two iron oxides are stable : hematite (Fe_2O_3) and magnetite (Fe_3O_4). A duplex scale made of an inner magnetite layer thicker than the outer hematite layer is usually reported (Fig. 1) [2].

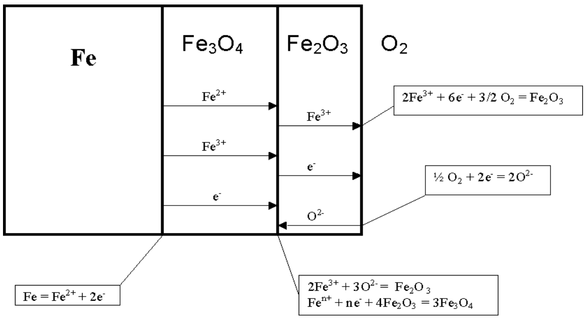

Fig. 1 : *Iron oxides duplex scale formed below 570°C : interfacial reactions and diffusion [3].*

The structure of the magnetite layer favours cationic transport through the scale. However, Fe and O have similar diffusion coefficients in hematite, and it is not clear which species is likely to be rate controlling during film growth [4].

In order to model scale growth over long time, it is essential to characterise the nature, the morphology and the microstructure of the oxide scales. Particular care has been brought to determine grain sizes because at these low temperatures grain boundary diffusion could play an important role.

Several experimental means have been implemented. The oxidation tests have been performed in a thermobalance or in a classical furnace under a controlled atmosphere. Oxide scales have been characterised using SEM, TEM and X-Ray diffraction. Then, Oxide scales formed were fractured and their morphologies were investigated using SEM.

1-1 Experimental Procedure

Specimens Preparation. Every sample is taken from an ARMCO iron sheet, the composition is given in Table 1. These specimens ($30*10*2\ mm^3$) were mechanically polished using 1200 grit SiC paper, then cleaned in alcohol , dried and left for about 3 days in an ambient atmosphere.

Table 1 : *Composition of iron samples used for experiments (% weight)* .

	C	Mn	Si	S	P	Ni	Cr	Mo	Cu	Sn	Al	N
ARMCO	0.001	0.05	0.01	0.003	0.004	0.019	0.013	0.001	0.005	0.002	0.001	0.003

Thermogravimetric Analysis. Oxidation treatments were performed in a "SETARAM TAG 24" thermobalance. The accuracy of this thermobalance is better than 5 µg at all temperatures. Furnace temperatures are controlled using Pt/Pt-Rh 10% thermocouples with an accuracy better than +/- 1 °C. The oxidation tests were performed between 260 and 500 °C under a mixture of dry air and H_2O vapour (2 vol%) flow. Furnace rising temperature speed is 10°C/min under reducing gas flow (He). After stabilization for 2 hours at the test temperature, the oxidant mixture flow rate is fixed at $2.3\ l.hr^{-1}$. One different test has been performed in the same conditions but using dry air as oxidation gas at the temperature of 400°C.

Oxidation tests in a classical furnace. The furnace design allows the exposure of several samples to a controlled atmosphere at the same time. Specimens are introduced in a quartz tube in a furnace through which a $15\ l.hr^{-1}$ continuous flow of a mixture of air + 2 vol% H_2O is maintained.

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<u>Determination of parabolic rate constant k_p.</u> Assuming that the oxide scale growth follows a parabolic law, the parabolic rate constant (k_p) has been evaluated from weight gain measurement by using the most general expression for parabolic kinetics [5]:

$$t = a + b\Delta m + c\Delta m^2 \qquad (1)$$

where Δm is the weight-gain per unit area (mg cm^{-2}) and t the time (s). In Equation (1), the coefficient c is equal to the reciprocal of the parabolic rate constant k_p ($mg^2.cm^{-4}.s^{-1}$), independent of the initial condition for integration of the rate equation [5]. Equation (1) could be fitted to the entire experiment to get a global value of k_p, or to local set of (t, Δm) data to evaluate if a stable regime is reached.

1.2 Growth Kinetics Results

Long-time thermogravimetric treatments (about 250 hours) have been performed at four distinct temperatures: 260, 300, 400 and 500°C. All experiments have been done in a mixture of dry air and 2% (vol) H_2O. An additional thermogravimetry analysis has been performed in dry air at 400°C. Fig. 2 compares weight gain per unit area versus time for two samples exposed 260 hours at 400°C in different atmospheres : dry air and air with 2 vol% H_2O. In both cases, the curve appears to be parabolic but the oxidation seems faster in dry air.

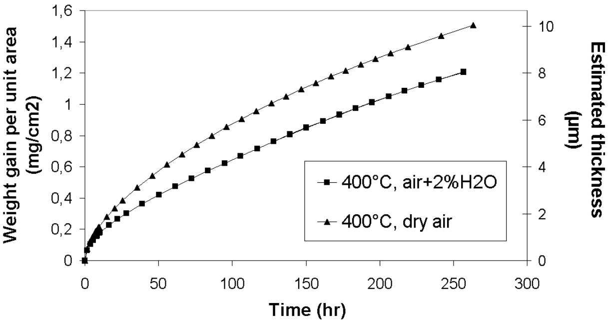

Fig. 2 : *Weight gain curves obtained during isothermal oxidation at 400°C under two different atmospheres: air + 2 vol% H_2O and dry air.*

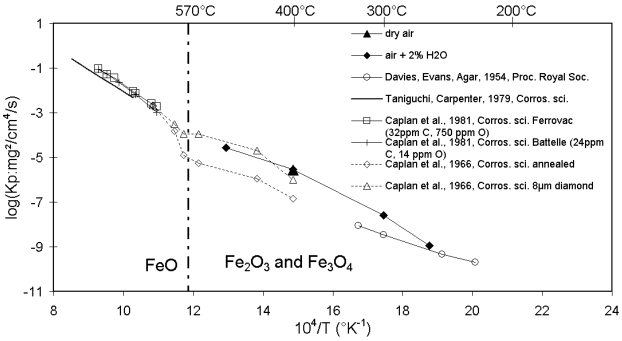

Fig. 3 : *Comparison of parabolic rate constants as a function of test temperatures (called "dry air" and "air + 2% H_2O") with those from the literature [6-9].*

The evaluation of parabolic rate constant (k_p) is made as described previously. Calculated values, after the transitory stage of faster oxidation kinetics, are compared with those from the literature in the Arrhenius plot presented Fig. 3. Even if the weight gain curve of iron oxidation in dry air is higher than the one obtained in air with 2 vol% H_2O, k_p values are close. Parabolic rate constants obtained in this work are in good agreement with data published by Caplan et al. in 1966 for polished specimens [9] and Davies et al. in 1954 at 260°C [6]. And it seems that annealed specimens lead to slower kinetics between 300 and 600°C. Moreover Davies *et al.* underline that only their kinetics obtained at 350°C follow a parabolic law.

1.3 Scale Morphologies.

<u>Surface scale morphologies.</u> Fig. 4 shows the evolution of the surface morphology of scales formed at temperatures between 300 and 500°C in air + 2 vol% H_2O. On samples treated at 300 and 400°C in wet air for 260 hours, there are many whiskers all over the surface. Voss and al. have observed such structures on iron oxides and shown the presence of a superdislocation or of a tunnel in some whiskers giving an easier way for cation diffusion to the surface [10]. Moreover, according to Rapp [11], whiskers formation is favoured in wet atmospheres and at low temperatures because surface diffusion needs to be faster than volume diffusion and oxidant molecule dissociation. Then this dissociation rate controls whiskers growth. At 400°C there are some areas where the whisker density is lower. At 300°C, the

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whiskers are longer but thinner than at 400°C. Diffraction in a TEM on a specimen oxidised at 300°C for 260 hours has shown that whiskers have a hematite structure [12]. The surface of the scale obtained at 500°C in wet air presents two different morphologies: areas with whiskers as seen at lower temperature, and areas where crystallites are round-shaped. The observation of a sample oxidized at 300°C for 1000 hours in wet air (Fig. 4(d)) exhibits two different morphologies as seen on sample oxidised 28 hours at 500°C.

The observation of the surface of a specimen oxidized at 400°C in dry air shows that the main difference between the two atmospheres (dry air and air + 2 vol% H_2O) at 400°C is the total absence of whiskers on the surface of the scale obtained in dry air.

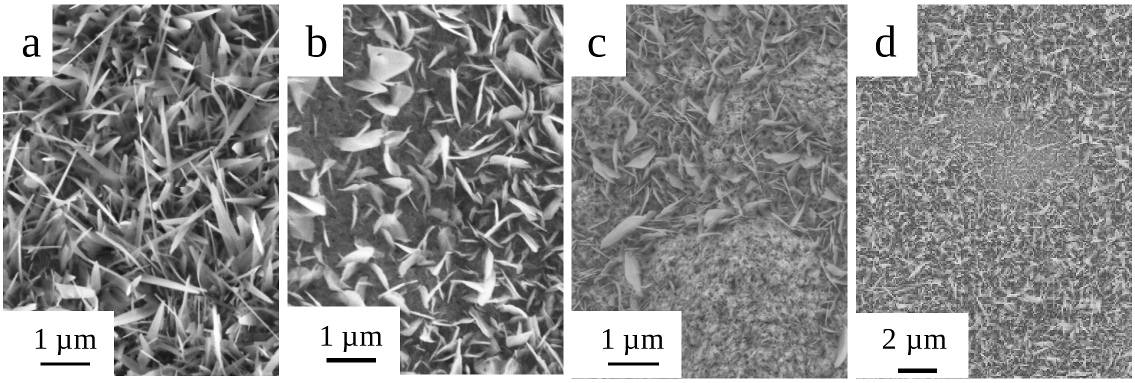

Fig. 4 : *Evolution of iron oxide surface morphology formed in air + 2 vol.%* H_2O *at different temperatures : (a) 300°C, 260hr, (b) 400°C, 260hr, (c) 500°C, 28hr, (d) 300°C, 1000hr.*

Microstructure of fractured oxide scales. Some observations of fractured cross-sections of iron oxides formed at 400°C are given in Fig. 6. At 300, 400 and 500°C, whatever is the atmosphere, three-layered scales exhibit three distinct microstructures. Table 2 summarizes the microstructural characteristics of each of the three layers for the different specimens.

Both specimens oxidized at 300 and 400°C for 260 hours show columnar grains in the middle of their scales. Even if there is a great difference between the scale thickness, the microstructures are similar, but with a typical grain size of 100 nm at 300°C and of about 200 nm at 400°C. Tests performed at 400 and 500°C allow the comparison of the microstructures of scales of the same thickness despite the different temperatures. In this case, the outer layer is thin (300 to 500 nm) and composed of equiaxed grains. The middle layer is made of columnar grains of about 400 nm diameter showing porosities of about 100 nm in the upper part of this intermediate layer. This is illustrated on Fig. 5(c). The inner scale is composed of smaller columnar grains than the middle layer (Fig. 5(b)).

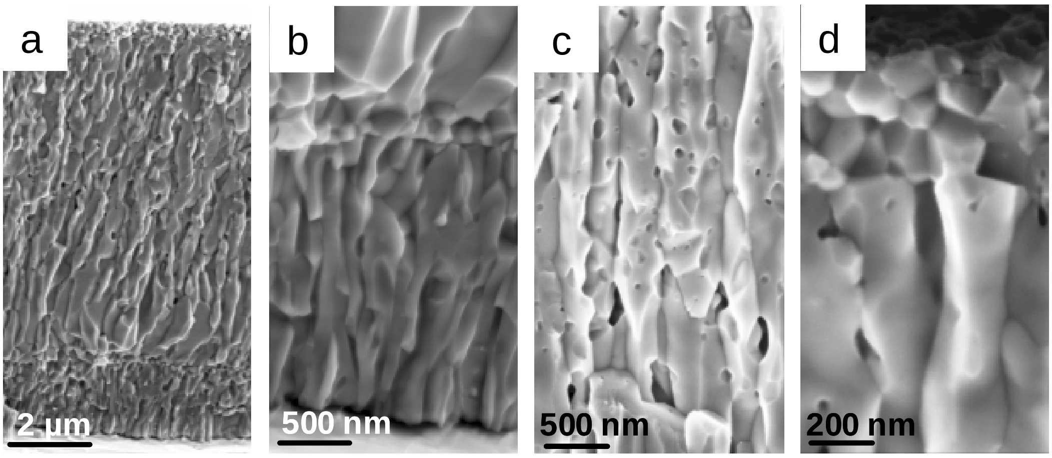

Fig. 5 : *Fractured cross-section of iron oxides formed at 400°C in 260 hours : (a) global view of the scale, wet air, (b) inner layer, wet air, (c) middle layer, dry air, (d) outer layer, dry air.*

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A decohesion between the inner and middle layers has been observed several times on 300°C and 400°C oxidized samples. The origin of this phenomenon has not yet been investigated but it does not seem to be due to the fracture of specimens for observation because it has also been observed on polished cross sections. This could happen during the furnace cooling or be due to growth stress during oxide scale growth. An alternative explanation could be an accumulation and condensation of vacancies at this particular interface during the scale growth.

At 400°C, contrary to surface morphologies, there is not much difference between samples oxidized in wet or in dry air in scale fracture morphologies.

Some X-Ray diffraction analyses made on different samples, with two incidence angles, show that hematite layer is laying over the magnetite layer. Considering the microstructure of scales and previous studies it seems reasonable that the two inner layers made of columnar grains are magnetite and that the outer layer made of equiaxed grains is hematite, as verified by diffraction on isolated whiskers.

Table 2 : *Characteristics of iron oxide scales formed during different oxidation treatments.*

	300°C 260 hours air + 2% H_2O	400°C 260 hours air + 2% H_2O	400°C 260 hours dry air	500°C 28.4 hours air + 2% H_2O
Surface morphology	Whiskers	Whiskers	Round crystallites	Whiskers + round crystallites
Outer layer of the scale	Fine grains e~150 nm	Equiaxed grains d~100 nm e~300 nm	Equiaxed grains d~100 nm e~300 nm	Equiaxed grains 100<d<300 nm e~800 nm
Middle layer of the scale	Small columnar grains d~100 nm e~650 nm	Columnar grains Porosity in the upper half part d~300-600 nm e~10 µm	Columnar grains Porosity in the upper half part d~400 nm e~12 µm	Columnar grains Porosity in the upper half part d~500 nm e~10 µm
Inner layer of the scale	Fine grains e~200 nm	Fine columnar grains e~1 µm	Fine columnar grains e~1 µm	Fine columnar grains e~1.8 µm
Scale thickness measured on micrographs	~ 1 µm	~ 10 - 13 µm	~ 13 - 14 µm	~ 11 - 13 µm
Scale thickness estimated from mass gain	1 µm	9 µm	10 µm	14.4 µm

1.4 Conclusions on the experimental study

Long duration oxidation experiments have been performed on iron at low temperature in dry air and wet air. The parabolic rate constants measured are in relatively good agreement with previous studies and differences have been attributed to the effect of sample preparation (no annealing prior to oxidation). A comparison of iron oxidation in dry air and in a mixture of air with 2 %vol. H_2O at 400°C shows that the weight gain is greater in dry air. This phenomenon is probably due to the transitory states because parabolic rate constants are similar. Evolution of iron oxide scale surface morphology has been studied as a function of experiment duration and temperature. The surface of oxide formed in dry air shows no whiskers. At every temperature, oxides obtained in wet air are covered by whiskers but there is an evolution: first, the whole surface is covered and then it seems that the oxide scale grows between the whiskers so that there are two distinct morphologies on the surface of iron oxide scales: whiskers and round-shaped crystallites. Whatever the temperature and the total scale thickness, in wet and dry air, the iron oxide scales are three-layered composed of an equiaxed grained outer layer probably made of hematite, a thick middle layer and a thin inner one, both made of columnar grains forming a magnetite duplex scale. It seems that the two extreme layers develop first, but this must be investigated further.

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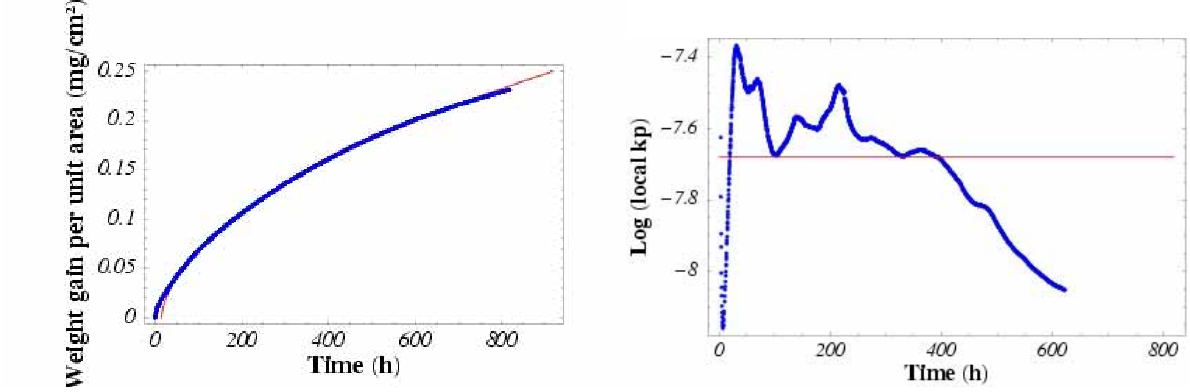
2. Oxidation Modelling

Two complementary approaches of modelling of dry oxidation in the typical temperature range concerned by containers in long term interim storage have been considered. First, a basic models consists extrapolation over long time of experimental data,. following simple analytical laws deduced from Wagner's classical oxidation theory based a simple control of the oxide scale growth by volume diffusion in the scale. Second, the development of a numerical model able to take into account expected governing mechanisms at low temperature, like partial interfacial control of the oxidation kinetics and/or grain boundary diffusion, is under progress.

2.1 Basic model

We have used experimental kinetics results obtained on iron to build a first basic model assuming that the oxide scale growth follows a parabolic law ($w^2 = k_p\ t$). A simple extrapolation to a 100 year period of our data leads to the formation of an oxide layer due to dry oxidation thinner than 1µm at 100°C and 60 µm at 300°C. These calculations show that dry oxidation of iron could be very low but they assume that the layer does not spall away and that the corrosion mechanism is the same for all the storage period and in particular that there are no changes in the temperature and atmosphere composition (no pollutant).

To assess for long time prediction this basic model based on the assumption of a constant k_p parameter, a thermogravimetric experiment performed at 300°C has been extended over a 800 hours duration and scanned with the local k_p analysis proposed in [5] (Fig. 6).



a) *b)*

Fig. 6 : *a) weight gain curve during long time isothermal oxidation of iron at 300°C under air with 2% vol. H_2O;b) evolution of local k_p versus time for the corresponding oxidation kinetic curve from the methodology proposed by Monceau and Pieraggi [5].*

As can be seen in Fig. 6b during the first steps of the oxidation process, the local parabolic rate constant has a large increase. It could be the effect of the transitory state. Then local k_p oscillates around a global k_p value represented by the horizontal line on Fig. 6b. Finally, after about 350 hours, the local k_p decreases. Such an evolution of the parabolic rate constant could be due to an evolution of cross scale diffusion parameters.

Remind here that the classical parabolic law commonly used in oxidation is deduced from Wagner's model developed between the 30ies and the 70ies, whose most specific hypothesis are :

- a pure cationic (or pure anionic) transport with constant diffusivity in the scale
- fixed equilibrium concentrations at interfaces
- and the classical steady state approximation.

On this basis, 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. [13] and Bastow et al [14] 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 [15], grain boundary diffusion [16].… 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) as evidenced by kinetics evolution shown at long duration in our experiments, by 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. Moreover, several others phenomena should play a major role in the oxidation rate at low temperature. First, as diffusion along grain boundaries can be the major transport mechanism, grain size distribution 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. 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 [17], Larose and Rapp outline the importance of these latter phenomena.

2.2 Advanced model

A numerical model able to reproduce all the major mechanisms presented above in order to have a more powerful tool to describe the oxidation rate over long periods is currently under development. 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 which is directly linked to the elimination of vacancies at the metal/oxide interface. 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. 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 [18].

The “1D” system under consideration can be described as a “sandwich-like” schematic image composed of a metal layer, 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;

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.

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To simulate the evolution of the 1D system, we calculate the concentration profiles evolution of the different species by solving Fick equations using a discrete contiguous slabs description of the system (Fig.7) and an explicit finite difference algorithm with fixed equilibrium conditions at moving interfaces. In the metal, the conservation equations is evaluated considering fluxes due to volume diffusion but also eventually a local rate of change in vacancy composition due to vacancy creation or annihilation by a uniform dislocation density following treatment proposed by Martin and Desgranges [19]. This work has also 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. The complete algorithm for numerical treatment of the interface motion is described in [20] 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.

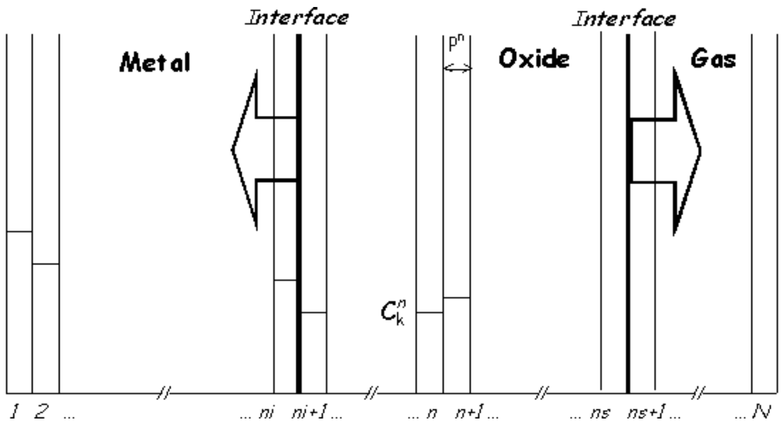

Figure 7 : *Schematic representation of the concentration profile used for the numerical resolution of the model*

Details results of first calculations completed with this model have been presented elsewhere [21].To illustrate some future applications that the model will enable, we presented here calculations for an intermediate assumption for vacancy treatment, considering that 80% of the incoming cationic vacancies at the metal/oxide interface are eliminated, and the rest being injected in the metal. The set of chosen input parameters is as follows : For boundary conditions at both interfaces, fixed equilibrium vacancy concentrations are chosen; The oxide lattice volume is taken twice the metal lattice volume and last, the kinetics parameters have been chosen to reproduce an oxide scale with a mixed anionic/cationic growth.

All the results are given taking the middle of the metal as reference. Figure 8a compares the calculated evolution of interfaces positions with a simulation done with the same set of parameters but considering that all cationic vacancies are injected in the metal. The growth rate is identical in the two cases, but the oxide position is shifted towards the middle of the metal in the case of elimination of cationic vacancies at the interface which induces elimination of lattice sites. For the same reason, in the case of injection of all incoming vacancies in the metal, the motion of the metal/oxide interface is only a result of inward oxygen diffusion. As expected from the chosen initial and boundaries conditions, the scaling rate is parabolic.

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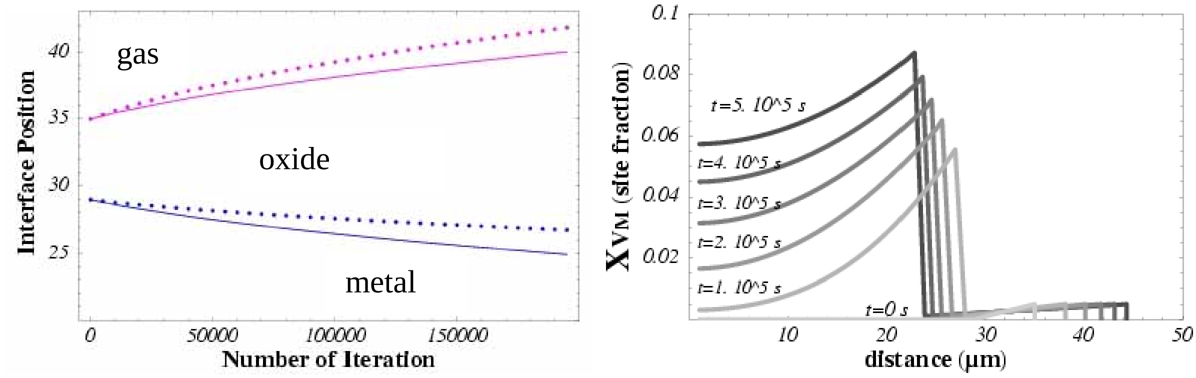

a) *b)*

Figure 8 : *a) Evolution of interface position in course of the numerical growth calculation: Interface metal/oxide in blue, surface in pink, with a part of cationic vacancies being eliminated at the metal /oxide interface (solid lines), with no elimination of vacancies at the interface (dotted lines) b) Evolution of the metallic vacancies concentration profile in the metal and in the oxide at different times of simulation.*

Figure 8b shows the evolution of metallic vacancies. As a result of fixed equilibrium conditions at the interfaces, the vacancy profiles in the oxide stay linear during the oxide growth. In the metal, the vacancies profiles quickly evolve as a consequence of the injection of a part of the incoming cationic vacancies at the metal/oxide interface in the metal. The shape of the vacancies concentration profile in the metal, in case of injection, suggests that growth of the oxide lead rapidly to oversaturation of vacancies in the metal and therefore to voids formation, as no sink strength is present in the metal. The next step will be to use the model with a non-null density of vacancy sink strength in substrate to evaluate the influence of the non-conservation of vacancies in the bulk on the metal oxidation rate. A partial interfacial control of the oxidation kinetics linked to the interface ability to eliminate vacancies will be also added. In a second phase, diffusion via short-circuits will be introduced.

Conclusion

In the framework of the COCON programme, two different approaches for the modelling of the dry oxidation kinetics are proposed. A basic model consists in some extrapolations of available experimental data in the temperature range of interest following parabolic laws deduced from classical oxidation theories. It leads to very small oxide scale and so to a very small metal loss even for extrapolations over 100 years. However measurement of growth kinetics on iron at low temperature show that the parabolic constant decreases with time at long duration, which suggests that parameters controlling growth rate evolve with time. Indeed in the temperature range concerned by long term interim deposit of waste containers, several mechanisms can control the oxidation rate : 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. A numerical model able to take in consideration several growth mechanisms is thus in progress. The model is based on an original numerical treatment to correctly and easily describe elimination of incoming cationic vacancies at the interface and thus relative motion between the substrate lattice and the oxide lattice, even for non-stationary states. In parallel, an experimental study is engaged to evaluate some input parameters for the future developments of the model like typical grain size of the oxide at low temperature, but also to get a better understanding of the scale growth mechanism. Some first important results have been obtained on the evolution of scale morphologies with oxide thickness for scales formed in the typical temperature range concerned by containers in long term interim storage (between 100°C and 400°C).

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