

Dry Oxidation Behaviour of Metallic Containers during Long Term Interim Storages

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Abstract – Low-alloyed steels or carbon steels are considered candidate materials for the fabrication of some nuclear waste package containers for long term interim storage. The containers are required to remain retrievable for centuries. One factor limiting their performance on this time scale is corrosion. The estimation of the metal thickness lost by dry oxidation over such long periods requires the construction of reliable models from short-time experimental data. Two complementary approaches for modelling dry oxidation have been considered. First, basic models following simple analytical laws from classical oxidation theories have been adjusted on the apparent activation energy of oxidation deduced from experimental data. Their extrapolation to long oxidation periods confirms that the expected damage due to dry oxidation could be small. Second, a numerical model able to take in consideration several mechanisms controlling the oxide scale growth is under development. Several preliminary results are presented.

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, 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 programme [1].

Modelling Oxidation

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 one. 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, that is to say Wagner's model, have been derived from experimental data on iron and on low-alloy steel oxidation tests. In a second step, in order to increase the reliability of the long term extrapolations from basic models, a non-steady state numerical model able to take into account several elementary steps is build. The aim is to get a more reliable tool to describe mechanisms that control scale growth in this specific low temperature range (in the field of oxidation).

BASIC MODEL

Experimental Measurements

Only a few studies dealing with iron and steel oxidation in the temperature range concerned by containers in long term interim storage (between 373K and 623K) 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 with iron and a low-alloy steel have been performed in wet air (2 vol.% H₂O) (reference atmosphere) under atmospheric pressure for several hundred hours. We have used these results to build a first basic model assuming that the oxide scale growth follows a parabolic law ($w^2=k_p t$). The constant k_p has been evaluated from mass gain measurements (w) or oxide scale thickness evaluations. Our values are in good agreement with those from literature (Fig. 1).

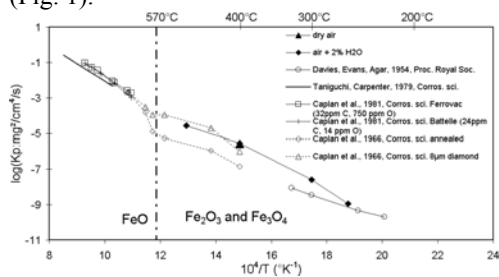


Fig. 1. Comparison of parabolic rate constants as a function of test temperatures (called “dry air” and “air + 2% H₂O”) with those from the literature.

Extrapolation

Assuming that diffusion phenomena in the scale, that control the oxidation rate remain constant during the whole storage period, an extrapolation of our data to a 100 year period leads to the formation of an oxide layer due to dry oxidation thinner than 1 μm at 373 K and 60 μm at 573K. 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).

Assesment of the basic model

Moreover, oxidation kinetics measured by thermogravimetry during long time experiment (a few hundred hours) do not follow parabolic law during all the tested period showing that a simplified parabolic model cannot be sufficient to represent oxidation phenomena over a long period. A local analysis of the mass gain curve shows that the parabolic rate constant k_p decreases with time (Fig.2) suggesting that the parameters which control the scale growth evolve with the time. Several phenomena should

play a major role in the oxidation rate at this temperature.

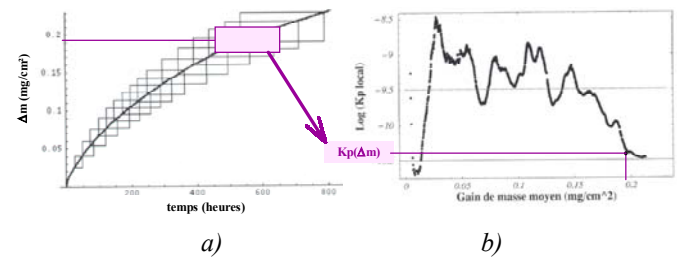


Fig. 2. a) Weight variations of an iron specimen oxidized at 573 K under air with 2 vol.% H₂O; b) Evolution of local k_p for the corresponding oxidation kinetic curve from the method proposed by Monceau and Pieraggi [5].

First, as diffusion along grain boundaries can be the major transport mechanism, the 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 [6], Larose and Rapp outline the importance of these latter phenomena. In addition, experimental results on the low-alloy steel 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 oxidised species.

ADVANCED MODEL

In order to have a more powerful tool to describe the oxidation rate over long periods a numerical model able to reproduce all the major mechanisms presented above is currently under development.

General description of the model

An overview of the different steps that we wish to treat in the final model is as follow :

- 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 to say,

whether the oxidation reaction is considered to be instantaneous or not, in respect to the diffusion.

iii) the annihilation or creation of point defects ;

iv) the electronic fluxes, effect of high field on migration, and electron tunnelling.

At the present stage of development, only vacancies have been taken into account as defects. In the oxide we can distinguish two types of vacancies, anionic and cationic. Only the point defect diffusion is treated. Finally, we shall not at this stage introduce mechanisms described in iv) that will be rate determining steps for thin oxide scales.

Description of the Numerical Method

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

In each layer we define the different species concentrations. The chemical species are the metallic species A and B, and an oxidant species O. In addition, in order to introduce effects like the influence on the scaling rate of defects annihilation (or creation), defects profiles will be calculated. In fact, diffusion coefficient of chemical species being proportional to defects concentration, scaling rate will be affected by the rate of defects annihilation (or creation) on sinks (and sources) in the metal which can be attributed to a density of dislocations. Furthermore explicitly calculating vacancy profile allows to point out the risk of scale detachment in case of local over-saturation of vacancy concentration near the interface.

To simulate the evolution of the 1D system, we calculate the concentration profiles evolution of the different species by solving Fick equations using 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 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 [7]. 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. 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.

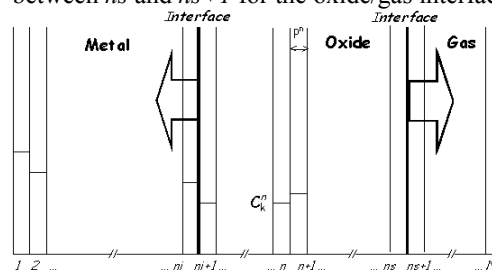


Fig. 3. Schematic representation of the concentration profile used for the numerical resolution of the model.

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 [8] 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.

Results

As the first step of this work, the model has been used considering a null density sink strength in the metal and has been numerically solved using $N=100$ or 300 slabs. Kinetic parameters have been chosen to reproduce an oxide scale with a slightly larger anionic mobility than cationic mobility. At the metal/oxide interface, two drastic and opposite treatment can be chosen : considering that all cationic incoming vacancies are annihilated at the interface or considering that all incoming vacancies are injected in the metal. We present here the results for the severest case for risk of scale detachment by vacancies oversaturation : all incoming vacancies are injected in the metal.

It has been verified that, as expected from the chosen fixed equilibrium conditions, the scaling rate is parabolic. Fig. 4a shows the associated evolution of metallic vacancies profile 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 figure 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.

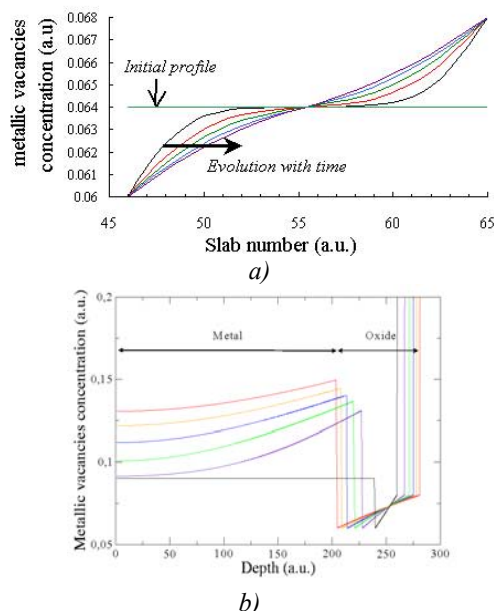


Fig. 4 : Evolution of the metallic vacancies concentration in the oxide and the metal *a)* for the first time steps (transition stage) and *b)* for long time simulation (stationary state) in the extreme case of conservation of vacancies.

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.

Future developments

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 in the metal on oxidation rate.

In a second phase, diffusion via short-circuits in the oxide will be introduced by defining in each discrete oxide slab a density of shortcuts. A related experimental study is in progress to have a good evaluation of grain sizes for oxide scales formed at low temperature.

CONCLUSION

In the framework of the COCON program that deals with the corrosion of waste containers in long term deposit, two different approaches of modelling of dry oxidation rates are proposed. The basic model consists in some extrapolations of available experimental data in the temperature range of interest following simple analytical laws deduced from classical oxidation theories. This leads to a very small oxide scale and thus to the loss of very small amounts of metal even for extrapolations to over 100 years. However, the reliability of this kind of basic models is very poor since it is based on the assumption that a single elementary process controls the oxidation rate. Indeed in the temperature range concerned by long term interim deposit of waste containers, several mechanisms can control the oxidation rate. A numerical model able to take in consideration several growth mechanisms is now in progress. At this stage of development, the originality of the proposed advanced model consists in explicitly calculating the vacancy profiles and treating these as non-conservative species. Hence, the model should be able to reproduce various phenomena proposed to explain well known effects on oxidation behaviour but often not introduced in other models, as for instance cold working of metal.

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