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Franck Ledoux, Françoise Valdivieso, Michèle Pijolat, Michel Soustelle, A. Frichet, et al.. Kinetic study of the oxidation by water vapour of a zirconium based alloy: Recrystallised Zircaloy-4. 5th International Symposium on High Temperature Corrosion and Protection of Materials, May 2000, Les Embiez, France. pp.223-230. hal-00409908

HAL Id: hal-00409908
https://hal.science/hal-00409908

Submitted on 13 Aug 2009

5th International Symposium on High Temperature Corrosion and Protection of Materials, Les Embiez, 22 au 26 mai 2000

# Kinetic study of the oxidation by water vapour of a zirconium based alloy: Recrystallised Zircaloy-4

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Keywords :

*Zirconium alloy, oxidation kinetics, water vapour, pre-transition*

## Abstract:

The oxidation of a zirconium based alloy (recrystallised Zircaloy-4) has been studied at 500°C, by thermogravimetry under controlled partial pressures of water vapour and hydrogen. The study is restricted to the pre-transition state of oxidation, the aim being to identify the rate-limiting step of the oxide growth. It has been verified experimentally that the system is in a steady state during the pre-transition period. Moreover, using a method based on the isolation method, it has been shown that the oxidation could be described by a single rate-limiting step only when a weight gain of 7.5 $mg.dm^{-2}$ has been reached. Since the kinetic curves are not parabolic, a diffusion model has been proposed, which takes into account the effect of barriers on the diffusion (such as pores, blisters, cracks... in the oxide layer) and which is in good agreement with the experimental curves. Then, numerical fitting has shown that the beginning of the oxidation could be interpreted by a mixed reaction-diffusion steady solution, which tends towards a single diffusion rate-limiting step when the oxide layer is thick enough (about 0.5 µm).

## 1. INTRODUCTION:

Zirconium based alloys are widely used as cladding material of fuel rods in water-cooled nuclear reactors, because of their good mechanical properties, their low corrosion rate and their low cross-section for absorption of thermal neutrons. Unfortunately, these alloys undergo a kinetic transition, which is a sharp increase in the oxidation rate when the oxide thickness exceeds a critical value [1]. Despite the large amount of work which has been carried out up to now, the oxidation mechanisms of zirconium alloys in presence of water vapour are not well established yet, specially from the kinetic point of view.

The present study is restricted to the pre-transition state, in which the oxide growth is generally assumed to be rate-controlled by a diffusion step through the oxide layer (despite the fact that the shape of the oxidation curves is not strictly parabolic) [1,2].

In this paper, we present the first results of a kinetic study of the oxidation of a zirconium alloy, recrystallised Zircaloy-4, by water vapour, the final aim of the work being to identify the rate-limiting step of the oxide growth.

In order to propose a mechanism for the oxide growth, it is worth assuming that the growth mechanism consists in a series of elementary steps (interface steps (such as adsorption or interface reactions) and diffusion steps), and one of these steps is rate-limiting, the others being at equilibrium. The approximation of the rate-limiting step implies that (i) the system is in a steady state and (ii) that the oxidation rate is proportional to the product «$\Phi$.E», where $\Phi$ is the reactivity of growth of the oxide, (in $mol.s^{-1}.m^{-2}$), which depends on the physico-chemical variables (pressure P, temperature T, alloying elements...), and E is the « spatial function » ($m^2.mol^{-1}$), characteristic of the extent of the reaction zone where the rate-limiting step of the transformation occurs. E depends on the time and on the history of the solid from the beginning of the transformation up to the considered instant [3]. For example, in the case of a rate limited by the diffusion of a chemical species in the oxide scale due to a concentration gradient, Φ and E take the following expressions, for a plate having an initial thickness $2x_0$ and an area $s_0$:

$$\Phi = \frac{D.\Delta C}{x_0} \quad \text{and} \quad E = \frac{2\,x_0\,s_0}{x\,n_0} = \frac{V_M}{x}$$

where x is the thickness of the growing oxide, $n_0$ and $V_M$ are respectively the initial number of moles and the molar volume of the metal.

In this paper, we will show first that the two assumptions (i) and (ii) can be verified experimentally [3-5], which is necessary before going further in the kinetic modelling of the oxidation. Then, a rate law will be proposed to account for the shape of the kinetic curves.

## 2. EXPERIMENTAL:

The zirconium alloy, recrystallised Zircaloy-4, was supplied by CEZUS, its composition is given in Table 1. The samples were plates of 1cm by 1cm (or 0.3cm x 1cm for DSC experiments), 0.4mm thick; before the oxidation experiments, they were chemically polished in a fluoronitric solution (40% $HNO_3$, 4% HF, 56% $H_2O$) and then carefully washed with water.

| | % Sn | $O_2$ (ppm) | Fe (%) | Cr (%) |
|---|---|---|---|---|
| Zircaloy-4 | 1.3 | 1300 | 0.21 | 0.1 |

*Table 1: Alloy composition (recrystallised Zircaloy-4)*

The oxidation was followed by isothermal thermogravimetry at 500°C, under controlled partial pressures of water vapour (66.7hPa) and hydrogen (26.7hPa), the total pressure being 94hPa (static atmosphere, symmetrical balance Setaram MTB $10^{-8}$). The isothermal conditions are reached after 5 minutes (the atmosphere being established previously). The hydrogen pressure has been chosen about 10 times greater than the maximum hydrogen quantity released during the oxidation experiments, to ensure that the hydrogen pressure could be considered as constant during the experiments.

The experiments of simultaneous thermogravimetry and differential scanning calorimetry (DSC) were performed using a Setaram TG-DSC 111, at 500°C, under a flowing mixture of water vapour (13.3hPa), hydrogen (81.6hPa) and helium as a carrier gas (the total flowrate is $1l.h^{-1}$). The sample is in isothermal conditions after about 30 minutes (which is the time necessary to raise the temperature of the furnace from 20°C to 500°C, with a heating rate of 20°C/min).

## 3. EXPERIMENTAL RESULTS:

### 3.1. Shape of the kinetic curves:

An example of curve of weight gain (Δm) versus time is given in Fig. 1a, obtained at 500°C in static atmosphere ($P_{H2O}$=66.7hPa, $P_{H2}$=26.7hPa).

It can be verified easily if the curve is parabolic, by representing the weight gain Δm versus the ratio of the time t to the weight gain (t/Δm): this leads to a straight line in the case of a parabolic curve. Fig. 1b shows that the representation Δm=f(t/Δm) corresponding to the curve of Fig. 1a is not linear. This feature was observed on all the experimental kinetic curves, thus these curves are not parabolic, and they cannot be accounted for by a classical model of growth limited by a steady diffusion (nevertheless, if we assume that a power law describes our experimental results ($\Delta m^n = kt$), the value of n is about 2.4).

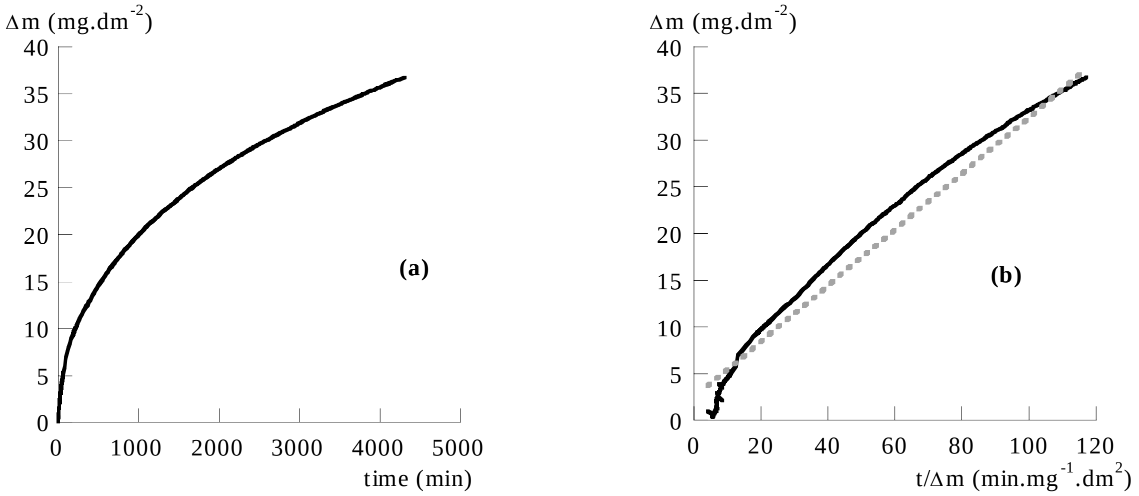


*Fig 1: (a) Curve of weight gain versus time for Zy-4, at 500°C ($P_{H2O}$=66.7hPa, $P_{H2}$=26.7hPa), and (b) corresponding representation of Δm versus t/Δm with a linear curve fit (dotted line).*

### 3.2. Steady state:

It can be shown [6] that when a system is in a steady state, the curves giving the reaction rate versus time, obtained with two different experimental techniques, are affine, the axis being the rate axis and the direction the time axis.

We have chosen to measure simultaneously the oxidation rate by thermogravimetry and calorimetry (heat flow, the standard enthalpy $\Delta H^0$ for the oxidation being about 600kJ.mol$^{-1}$ at 500°C). The curves of rate of weight gain and heat flow versus time have to be superimposed in two axis systems with different ordinate scales. Fig. 2 shows the curves obtained at 500°C for partial pressures of water vapour and hydrogen respectively equal to 13.3hPa and 81.6hPa.

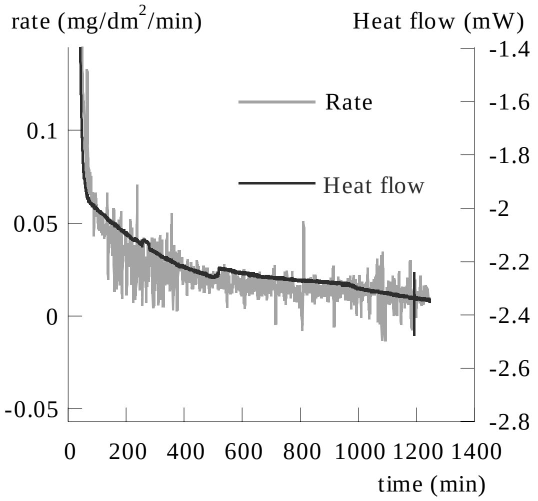


*Fig 2: Steady state test - Curves of rate of weight gain and heat flow at 500°C ($P_{H2O}$=13.3hPa, $P_{H2}$=81.6hPa).*

The sample is in isothermal conditions after about 30 minutes: from this time, the curves are superimposed correctly, and thus the assumption of the steady state is valid.

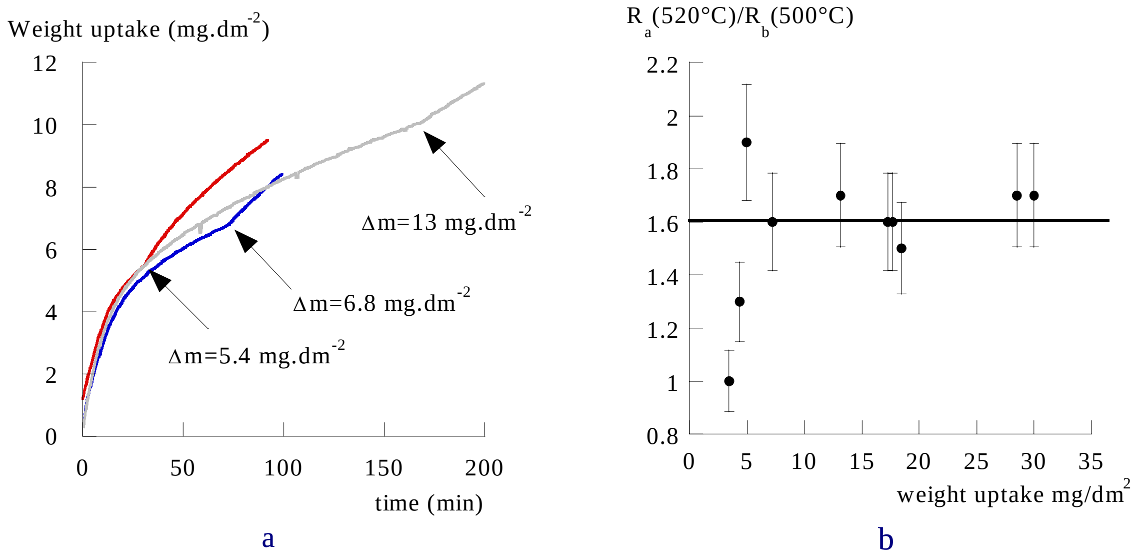
### 3.3. « Φ.E » test:

In order to verify the validity of the assumption (ii) (the oxidation rate $d(\Delta m)/dt$ is proportional to «Φ.E»), we have used the isolation method [7, 8], which consists into changing suddenly a physico-chemical variable (P, T) from a value $Y_0$ to a value $Y_1$, at a given weight gain. In practise, we have changed the temperature from 500 to 520°C, at various weight gains, the partial pressures of water vapour and hydrogen remaining constant ($P_{H2O}$=66.7hPa, $P_{H2}$=26.7hPa). Some experimental curves are given in Fig. 3a, the temperature changes being indicated by the arrows (the time to heat up the sample from 500 to 520°C is about 5 minutes).

Let be $R_{bi}(T_0, \Delta m_i)$ and $R_{ai}(T_1, \Delta m_i)$ the rates before and after the temperature change at a given weight gain $\Delta m_i$. If the assumption (ii) is valid, their ratio must be constant, whatever the weight gain at which the temperature is changed could be, according to Eq. 1:

$$\frac{R_{ai}(T_1,\Delta m_i)}{R_{bi}(T_0,\Delta m_i)} = \frac{\Phi(T_1)E(\Delta m_i)}{\Phi(T_0)E(\Delta m_i)} = \frac{\Phi(T_1)}{\Phi(T_0)} \qquad \text{Eq. 1}$$

The results of the test are indicated in Fig. 3b: taking into account the experimental error, shown by the error bars, (11% as determined from several experiments performed at the same weight gain), the ratio of the rates is constant from a weight gain of 7.5mg.dm$^{-2}$ (which corresponds to an oxide thickness of about 0.5µm). Thus, the initial stages of oxidation for Zy4 cannot be interpreted by a single rate-limiting step.



a b

*Fig. 3: (a) application of the isolation method for the « Φ.E » test: temperature changes at various weight gains, and (b) results of the test.*

It may be noticed that such a method, consisting into changing suddenly an experimental condition, has already been used in the case of Zircaloys : in these experiments, the pressure of oxygen [9, 10] or water [10] was changed, in order to study the effect of the gas on the oxidation.

## 4. INTERPRETATION:

### 4.1. Model of diffusion (when the « Φ.E » test is verified) :

It has been shown that the system is in a steady state from the beginning of the oxidation, but the « Φ.E » test is verified only when a weight gain of 7.5mg.dm$^{-2}$ has been reached. Thus, from that weight gain, it is possible to describe the oxide growth by a single rate-limiting step. Neither an interface step (which should lead to a linear rate law, in case of constant area with time of reaction) nor a diffusion step in the Wagner approximation (parabolic rate law) can account for the shape of the experimental curves.

A cause of departure from the parabolic equation was suggested by Mott and Cabrera [11], taking into account an electric field in the oxide film. This theory leads to an oxidation rate proportional to sinh($X_0/X$), where X is the oxide thickness and $X_0$ a constant ; but such an equation is not in very good agreement with our experimental curves.

So we have considered that diffusion could happen along preferred paths, referring to the work of Evans [12], who described the effect of barriers (blisters and pores) on the oxidation rate. Assuming that the barriers were distributed according to a Poisson law, he obtained a logarithmic oxidation rate law. Such a law is not in agreement with our curves, but the model of Evans was generalised by Cournil [13], who considered also some particular cases.

One of them is the case where only two kinds of potential barriers exist, the normal barriers corresponding to the diffusion jumps in a perfect crystal (activation energy E), and one kind of abnormal barriers characterised by a higher activation energy (E'>E). Let P(q,X) be the probability of finding q abnormal barriers on a diffusion path of length X. In order to precise the function P(q,X), we can assume that the barriers are distributed on a diffusion path independently one from another, according to a Poisson's distribution ; the probability P(q,X) is then given by:

$$P(q,X) = e^{-bX}\frac{(bX)^q}{q!} \qquad \text{Eq. 2}$$

where b is the average number of barriers per unit of length. Of course, it could be possible to choose another statistical distribution of the barriers (for example a normal distribution).

We also assume that the abnormal barriers are infinitely high (i.e. $E' \rightarrow \infty$), which means that the diffusion will be stopped in all the diffusion path containing at least one abnormal barrier. The diffusion can only happen along the paths which do not contain any abnormal barrier, and the calculation finally lead to a rate law given by Eq. 3, where X is the thickness of the oxide layer:

$$\frac{dX}{dt} = K_d\,\frac{e^{-bX}}{X} \qquad \text{Eq. 3}$$

where $K_d$ is a constant.

The experimental kinetic curves have been fitted using this law, from a weight gain higher than 7.5mg.dm$^{-2}$ (or X>0.5µm, the oxide thickness being evaluated from the weight gain). Two different experimental curves are represented in Fig. 4: it can be seen on these examples that the agreement is correct.

Thus, from a given weight gain ($\Delta m > 7.5$mg.dm$^{-2}$), the oxidation of the Zy-4 alloy under water vapour and hydrogen can be described satisfactorily by a rate-limiting step of diffusion, along preferred paths. The diffusion barriers could be any kind of defects in the oxide layer; for example, it has been observed that cracks, parallel to the metal/oxide interface, appear in the layer from the beginning of the oxidation [14].

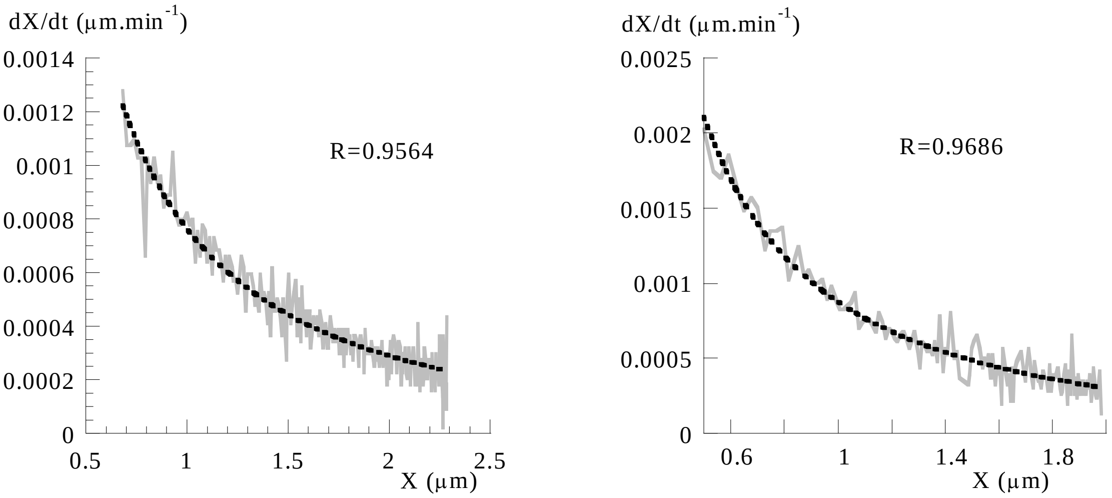


*Fig 4: Comparison between experimental curves (T=500°C, $P_{H2O}$=66.7hPa, $P_{H2}$=26.7hPa) and the diffusion law given in Eq. 3 (curve fit in dotted line).*

### 4.2. Initial stages of oxidation:

In the initial stages of the oxidation, the system is in a steady state, but since the «Φ.E» test is not verified, the assumption of a single rate-limiting step cannot be used. Consequently, we have considered a mixed reaction-diffusion steady solution, for which the rate R is such as:

$$\frac{1}{R}=\frac{1}{dX/dt}=\frac{1}{R_1}+\frac{1}{R_2} \qquad \text{Eq. 4}$$

where $R_1$ and $R_2$ are the solutions obtained assuming that either the interface reaction step or the diffusion step is rate-limiting.

In the case of an interface rate-limiting step, the rate $R_1$ is proportional to the product $\Phi_1.E_1$, which is constant with time: $\Phi_1$ does not depend on time since the system is in a steady state, and $E_1$ is constant for the oxidation of a platelet (assuming that the dimensions of the considered interface (external (between the oxide and the gaseous phase), or internal (between the metal and the oxide) do not vary with time). Thus, the rate $R_1$, which may depend on the temperature and the partial pressures of the gases as $\Phi_1$, is independent on time and it will be denoted $K_1$.

The rate $R_2$ is given by Eq. 3, and finally the mixed reaction-diffusion steady solution is:

$$\frac{1}{R}=\frac{1}{dX/dt}=\frac{1}{K_1}+\frac{X}{K_d\ e^{-bX}} \qquad \text{Eq. 5}$$

which leads to:

$$\frac{dX}{dt}=\frac{K_1\ K_d}{K_d+K_1\ Xe^{bX}} \qquad \text{Eq. 6}$$

and after integration, we obtain a relation (Eq. 7) between the time t and the thickness of the oxide layer X, which allows to compare easily the experimental curves to the calculated law:

$$t=\frac{1}{K_1}X+\frac{1}{K_d\ b^2}\left(1+(bX-1)\ e^{bX}\right) \qquad \text{Eq. 7}$$

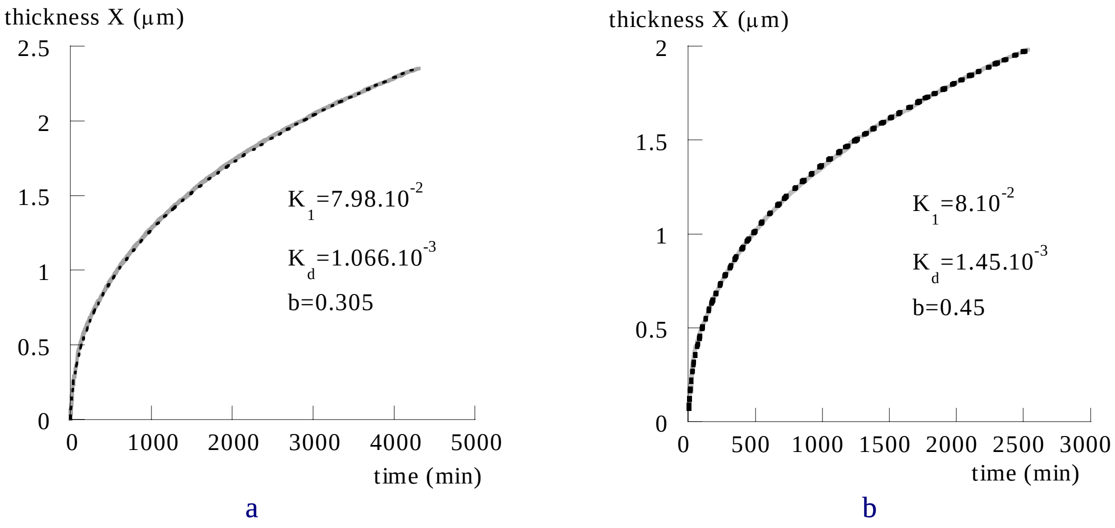


*Fig. 5: Comparison between experimental curves (T=500°C, $P_{H2O}$=66.7hPa, $P_{H2}$=26.7hPa) and the mixed reaction-diffusion steady solution (Eq. 7) (curve fit in dotted line).*

Several experimental kinetic curves have been fitted using the law given in Eq. 7: two examples are shown in Fig. 5a and Fig. 5b, it can be seen that the calculated curves are in a very good agreement with the experimental ones. It has been verified that these curves cannot be fitted with a parabolic law.

The relation t(X) in Eq. 7 is a sum of two terms in which the first one is related to the interface step and the second term to the diffusion step. From the curve fit, the values of the parameters K1, Kd and b are known, it is possible then to evaluate these two terms as a function of the oxide thickness X, as shown in Fig. 6 (the values of the parameters are those corresponding to the curves of Fig. 5a).

It can be noticed that the term due to the diffusion step becomes predominant compared to the interface term from about 0.5μm (greater than 100 times the interface term).

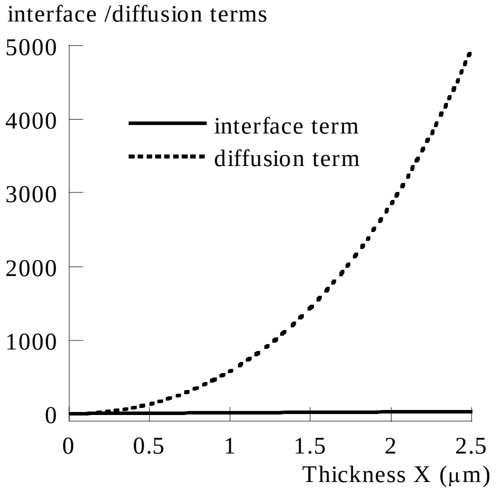


*Fig. 6: Comparison of the respective contributions of the interface term and the diffusion term, versus the oxide layer thickness (using the parameters given in Fig. 5a).*

Consequently, the oxidation kinetics of Zy-4 alloy can be described by a mixed interface reaction-diffusion steady solution, which tends towards a single diffusion rate-limiting step when the oxide layer is sufficiently thick. This is in agreement with the fact that the «Φ.E» test is not verified in the beginning of the oxidation (X<0.5μm); it becomes verified when the contribution of the interfacial step can be neglected.

In the diffusion model presented here, we have considered that diffusion occurred in the same way in the whole oxide layer, the curve fits giving an estimation of the parameter b. Nevertheless, it seems that the oxide film is a bilayered system [1, 15-16], with a porous outer layer, and a dense inner one (whose thickness increases during the oxidation, whereas the outer layer does not evolve significantly in pre-transition).

This bilayered structure has not been taken into account here, but in the model, the parameter b is a mean parameter, representative of the distribution of diffusion barriers (pores, cracks, ...) in the layer. It is difficult to know precisely the morphology and the thickness of these two oxide layers. However, the good adequacy between the experimental kinetic curves and the single-layer model developed here tends to show that this mathematical representation can be satisfactorily applied to the real system.

## 5. CONCLUSIONS

The oxidation of a zirconium alloy, recrystallised Zircaloy-4, has been studied in the pre-transition state, using an appropriate methodology in order to propose a rate law accounting for the shape of the experimental kinetic curves.

It has been shown that the system is in a steady state from the beginning of the oxidation, and the use of the isolation method has allowed to establish that a single rate-limiting step could not account for the initial stages of the oxidation, this assumption being only valid from a given weight gain.

Finally, a diffusion model has been proposed, taking into account some diffusion barriers in the oxide layer. Using this method, it has been concluded that the oxidation kinetics of recrystallised Zircaloy-4 could be interpreted by a mixed reaction-diffusion steady solution, which tends towards a single diffusion rate-limiting step when the oxide layer is sufficiently thick (about 0.5 µm in our experimental conditions).

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