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New approach to the kinetic modelling of high temperature corrosion of metals and alloys

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Abstract:

In this paper we present a new approach for the kinetic modelling of thermal transformations of solids. In the case of the corrosion of metals and alloys, the existence of a rate-limiting step is often assumed, which allows to account for the linear and parabolic kinetic curves (weight gain versus time), corresponding respectively to an interface and diffusion controlling step. But, in many cases, the reaction system is not so simple, thus we have developed a methodology in order to verify experimentally whether the kinetic assumptions of steady state and rate-limiting step can be applied. This is illustrated with two examples, leading to complex kinetic curves: the oxidation by oxygen of an Al-Mg 5% alloy in the liquid state (non reproducible curves), and the oxidation of Zircaloy-4 by water vapour (existence of a kinetic transition).

Introduction:

The kinetic modelling of the high temperature corrosion of metals and alloys is generally based on the identification of the rate-limiting step. Simple rate equations are frequently used as for example the parabolic or the linear rate law, which correspond respectively to an interface limiting step or a diffusion step through the oxide layer (in the case of plate-shaped samples). However in some cases the experimental kinetic curves do not fit any of the usual rate equations, which suggests that the oxide growth proceeds through an alternative kinetic behaviour. In order to analyse such complex situations, we propose a new approach principally based on the verification of the kinetic assumptions that most of authors are using *a priori*. This is illustrated by two examples: the corrosion of zircaloy-4 by water vapour and the formation of MgO from oxidation of Al-Mg 5% in the liquid state. It is also possible to apply it in the case of chemical transformations of powders (reduction of oxides by gases, thermal decompositions, ...).

The mechanism of oxide scale growth is assumed to consist in a series of elementary steps ; one of them is supposed to be rate controlling, the others being at equilibrium. This assumption implies that (i) the system is in a steady state and (ii) that the oxidation rate can be expressed by equation [1]:

$$\frac{d\xi}{dt} = n_0 \Phi.E \quad [1]$$

where ξ is the oxide amount, n_0 is the initial amount in metal, Φ is named the reactivity of growth of the oxide (it is a rate per unit of surface area, in $\text{mol.s}^{-1}.\text{m}^{-2}$), which depends on T , P_i (partial pressures), a_i (activities of alloying elements), and E is a function (in $\text{m}^2.\text{mol}^{-1}$) characteristic of the extent of the reaction zone where the rate-limiting step occurs (it depends on time, sample shape, ...). For example, in the case of a reaction 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 x_0 and an area s_0 :

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

where D is the diffusion coefficient, ΔC the difference in concentrations of the diffusing species at the two interfaces, x the thickness of the growing oxide, V_M the molar volume of the metal.

In this paper, we show first that the two assumptions (i) and (ii) can be verified experimentally, which is necessary before going further in the kinetic modelling of the oxidation. Then we propose a method of measurement of the variations of Φ with T and P_i . The first assumption (i) can be verified using simultaneous thermogravimetry and differential scanning calorimetry (DSC) (1-4). It can be shown easily (5) that when a system is in a steady state, the rates measured by two different experimental techniques should remain proportional at any time of the reaction.

The second assumption (ii) can be verified by experiments in which the temperature T or a partial pressure P_i is changed as suddenly as possible (T or P_i jumps). This method has been successfully used in previous works on various reaction systems (1-4, 6, 7), since it provides the extent of reaction in which equation [1] can be used. In practise, changes in temperature or partial pressure are carried out at various weight gains; it comes out from equation [1] that if the ratio between the rates before and after the T or P_i jump does not vary versus the weight gain (i.e. ξ), assumption (ii) is verified.

Finally, we describe an experimental method also based on temperature or partial pressure jumps which can be used to obtain directly the variations of the growth reactivity Φ with T and P_i .

In this paper, the methodology described above is used in the case of the oxidation of two alloys, in order to achieve a good understanding of the complex reaction systems and to propose reliable mechanisms:

- ❖ the oxidation by oxygen of an industrial Al-Mg5% alloy in the liquid state (2) : during the manufacture of these alloys, widely used in industry, the surface of the liquid metal may be oxidised, mainly leading to the formation of MgO (8). The mechanisms involved in this process have been studied in order to find a way to prevent oxidation. The kinetic curves being not reproducible, it was not possible to obtain directly from them the variations of the oxidation rate with the oxygen partial pressure, but the pressure jumps method allowed us to overcome these problems.
- ❖ the corrosion of Zircaloy-4 by water vapour (4) : 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 (9). Unfortunately, these alloys undergo a kinetic transition, which is a sharp increase in the oxidation rate when the oxide thickness exceeds a critical value. Despite the large amount of work dedicated to the oxidation of Zircaloy-4 by oxygen or water vapour (9-16), the mechanisms and the rate limiting step of the formation of zirconia are not well established yet. Due to the lack of consistent data on the effect of water vapour on the rate before and after the kinetic transition (11, 13, 15, 16), and in order to verify the validity of the assumptions generally used to account for the experimental results, it was thus decided to study the oxidation kinetics of Zircaloy-4 in water vapour. The aim of this work is to clearly put into evidence the differences between the pre- and post-transition domains from a kinetic point of view (existence of a steady state and of a rate limiting step in both domains, and variations of the growth reactivity Φ with water vapour).

EXPERIMENTAL

The aluminium-magnesium alloy is an industrial Al-Mg 5% alloy provided by Pechiney (purity about 99%). The samples are cylinders of 1mm height and 9mm diameter. Before each experiments, they were manually polished with 500 grade SiC and rinsed with acetone (the polishing method has no influence on the kinetic curves).

The zirconium alloy is a standard 0.41mm sheet of recrystallized Zircaloy-4 provided by Cezus, which was cut to 10x10mm platelets for gravimetric experiments and 5x15mm for TG-DSC experiments. The samples surface was cleaned first with an equimolar solution of ethanol and acetone in ultrasonic waves, then in pure ethanol and dried in compressed air.

The oxidation kinetics of both alloys was followed by isothermal thermogravimetry (symmetric thermoanalyser Setaram TAG 24), at atmospheric pressure, under a flowing mixture of helium and either oxygen or a mixture water vapour-hydrogen, the partial pressures being controlled by mass flowmeters Brooks 5850S (the water vapour pressure is fixed by a thermoregulated water bath, and measured by a humidity sensor Transmicor 241-242 Coreci). The oxidation conditions are reported in Table I for both alloys. In the case of Al-Mg5% alloy, the heating of the samples was carried out under oxygen at atmospheric pressure, since it was observed that a high oxygen pressure prevented the liquid alloy from oxidation: the oxygen pressure was held for 30 minutes at 1 atm at 700°C, then it was changed to the value chosen for each experiment.

Table I : Oxidation conditions for the Zy-4 and Al-Mg 5% alloys

	Temperature range	Pressure range
Zircaloy-4	500-530°C	Hydrogen : 10 hPa Water vapour : 13-80 hPa
Al-Mg 5%	700°C	Oxygen : 200-800 hPa

The experiments of simultaneous calorimetry and thermogravimetry were performed using a Setaram TG-DSC 111, under a flowing mixture of helium and the chosen gases. Micrographs were obtained on a scanning electron microscope Jeol JSM 840 for Al-Mg5% alloy, and DSM960A Zeiss for Zy-4.

RESULTS

Kinetic curves and oxide layer morphology

As shown in previous studies (17-19) for alloys containing more than 3% in magnesium, MgO is the first phase which appears during the oxidation, and it is the thermodynamically stable phase as long as the residual magnesium activity in the alloy is higher than 0.023, which corresponds to a weight increase of 1.7% (2). During the oxidation experiments, a thin solid MgO layer is formed when the temperature increases, and when the alloy melts, at about 648°C, it remains inside this solid layer which envelops the liquid metal. This layer undergoes strong deformations during the experiments, it is very rough and irregular. It appears quite different from one experiment to another, as shown by the SEM micrographs of figure 1, which represent the surface of two samples oxidised up to the same weight uptake (0.7%), in the same conditions of temperature and pressure ($P_{O_2}=400\text{hPa}$).

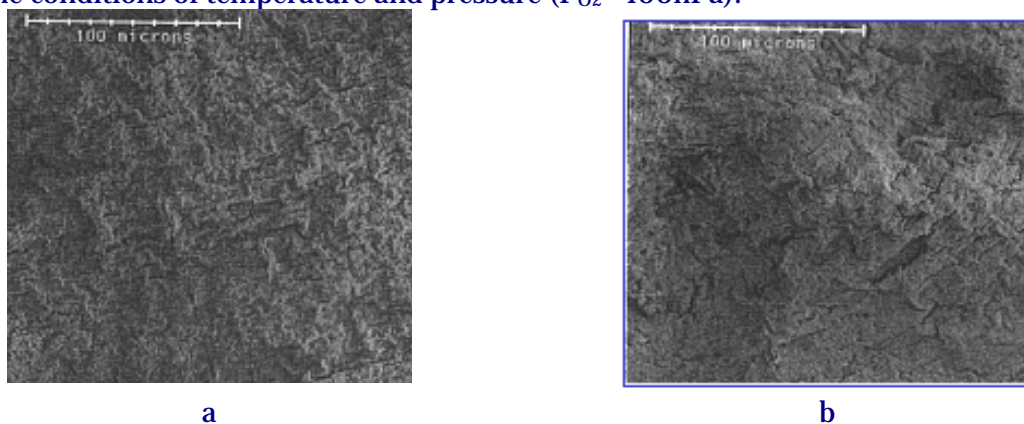


Figure 1: Surface morphology of two samples oxidised up to a weight uptake of 0.7% ($T = 700^\circ\text{C}$, $P_{O_2} = 400\text{ hPa}$).

SEM observations have also shown (2) that the oxide layer is formed of small MgO particles (about 0.5 μm); moreover, on other photographs not represented here (2), some holes are observed inside the samples, in which approximately cubic MgO grains are located (10 to 15 μm).

The various kinetic curves have the shape given in figure 2a (corresponding to an oxygen pressure of 400hPa): the curves are very irregular and not reproducible, which is not surprising since the samples undergo very important morphological changes during the reaction, which differ from one experiment to another.

In the case of the oxidation of Zircaloy-4, the isothermal (530°C) kinetic curves are shown in figure 2b, for two different values of the water vapour pressure (13 and 73 hPa, $P_{\text{H}_2}=10$ hPa). It can be observed that before the kinetic transition (characterised by an increase in the oxidation rate), the water vapour pressure has no effect on the oxidation, whereas it has an accelerating effect in the post-transition domain.

The cross-sectional views of the oxide scale grown during the pre-transition region present a continuous and uniform layer adherent to the substrate. Figure 3a shows a micrograph obtained with a sample oxidised during 4 hours at 530°C in 13 and 10 hPa of water vapour and hydrogen, respectively. The layer thickness calculated from the weight gain is 1.7 μm . No cracks connected to the gaseous atmosphere could be observed; the interface is more or less regularly undulated. Short cracks parallel to the interface appear regularly inside the layer.

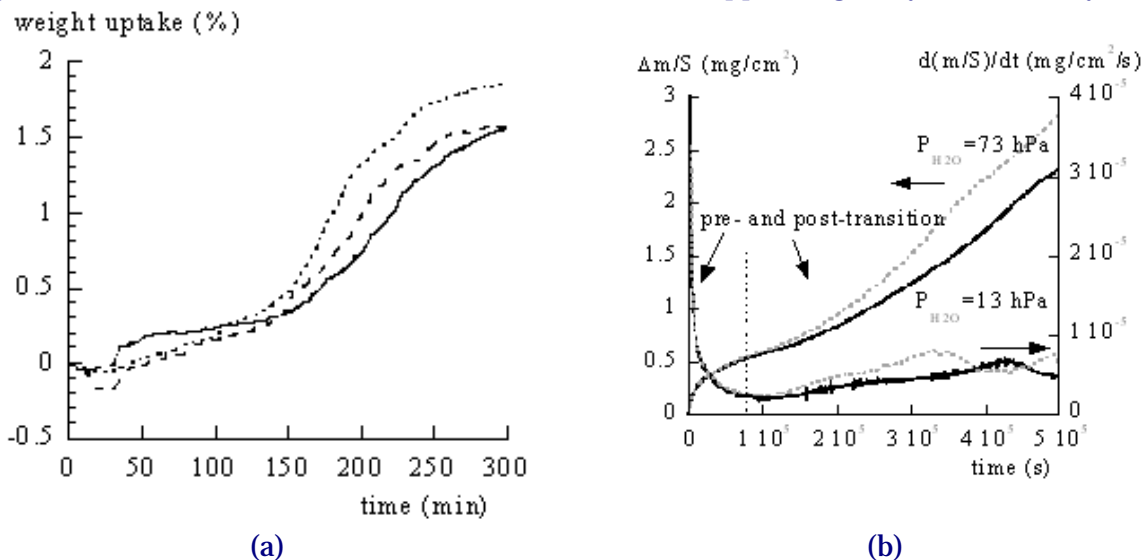


Figure 2: (a) Curves of weight gain and non reproducibility for Al-Mg5% ($T=700^\circ\text{C}$, $P_{\text{O}_2}=400$ hPa); (b) Weight gain and its derivative versus time for Zircaloy-4 ($T=530^\circ\text{C}$, $P_{\text{H}_2}=10$ hPa, $P_{\text{H}_2\text{O}} = 13$ hPa (continuous line) and 73 hPa (dotted line)).

Similar cracks exist in the samples obtained after the kinetic transition (figure 3b and 3c), but large cracks perpendicular to the interface and connected to the gaseous atmosphere are also observed. Moreover, these perpendicular cracks appear to be connected to parallel cracks, probably formed by the coalescence of the initial short ones and located at various depths under the surface (3.5 μm in figure 3b, 20 μm in figure 3c).

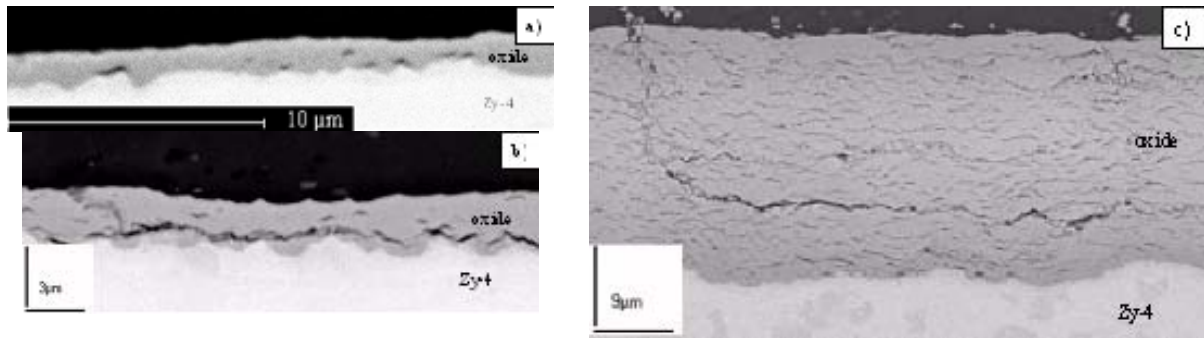


Figure 3: Cross sectional views of Zircaloy-4 samples oxidised at 530°C ($P_{H_2O}=13hPa$, $P_{H_2}=10hPa$) ; in pre- (a) and post-transition stages (b and c).

Steady-state assumption

We have chosen to measure simultaneously the oxidation rate by thermogravimetry and calorimetry (heat flow). The rates of weight uptake and heat flow versus time are represented in figure 4, for the Al-Mg 5% alloy (700°C, $P_{O_2} = 200hPa$) : a scaling factor allowing to superimpose the rate curves could be found after the first 80 minutes of the experiment (or $\Delta m=0.4\%$). During the temperature increase (10°C/min), the alloy melting (at about 648°C) induces a strong endothermic signal, which hides the exothermic signal due to the oxidation up to 80 minutes. Thus, the approximation of the steady state is valid at least from a weight uptake of 0.4%, i.e. a fractional conversion equal to 0.12 (the fractional conversion α is defined as : $\alpha = \frac{\Delta m(t)}{\Delta m_f}$, where $\Delta m(t)$ is the weight uptake at time t, and Δm_f is the weight uptake corresponding to the total consumption of the magnesium of the alloy, equal to 3.2% in our case (2)).

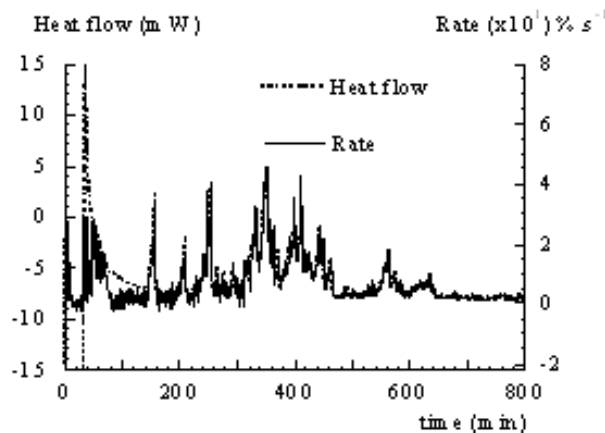


Figure 4: Rate of weight gain and heat flow versus time for Al-Mg 5% ($T=700^\circ C$, $P_{O_2}=200 hPa$).

A scaling factor could also be found for Zircaloy-4, in the pre- and post-transition stages, thus the steady state can be assumed (4). Nevertheless, the scaling factor is not the same in both domains, which remains unexplained.

Rate limiting step assumption.

The rate limiting step approximation means that the kinetics is controlled by the rate of one of the steps of the mechanism (elementary reactions like adsorption or interfacial reaction, and diffusion steps) and consequently the steady state is established. Then, equation [1] gives the variation of the rate with the time ($E(t)$) and the intensive variables (temperature, pressure,...). In isothermal and isobaric conditions, $\Phi(T, P, \dots)$ is constant, therefore a sudden change in T or P during an experiment will lead to a change in Φ only, while $E(t)$ will remain

approximately the same before and after the change. It comes out that the ratio of the rate measured on the right side of the change (Φ_r) to the rate measured on the left side (Φ_l) is simply equal to the ratio of $\frac{\Phi_r}{\Phi_l}$ according to equation [1]. So by doing a series of sudden changes at different times of reaction, the ratio of the rates will be constant as long as equation [1], or the approximation of the rate limiting step, is valid. Some experimental curves are represented in figure 5, in the case of the Al-Mg 5% alloy where the oxygen pressure was changed from 400 to 200 hPa (horizontal arrows), at various values of the fractional conversion. The result of this method, that we have called the « $\Phi.E$ » test, is represented on figure 6.

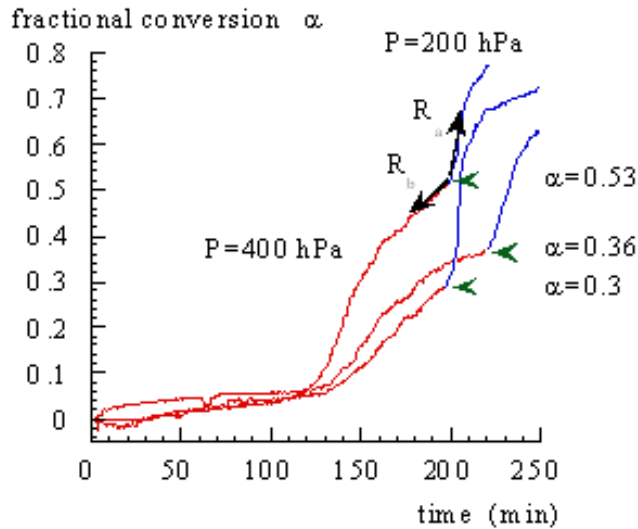
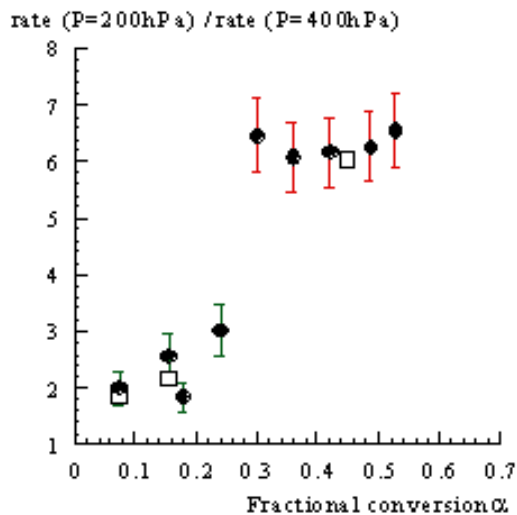
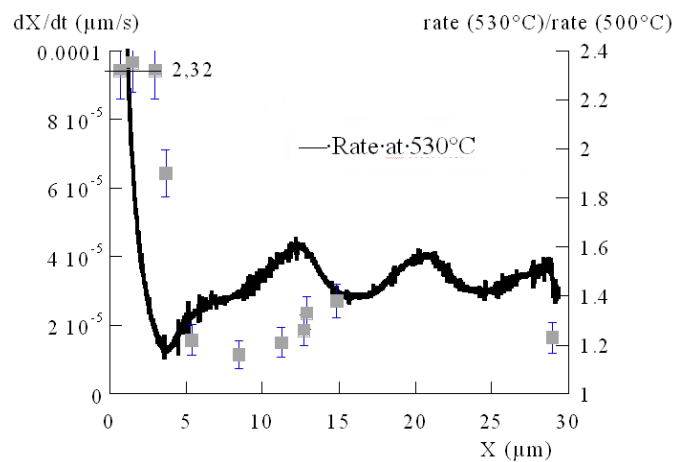


Figure 5: Oxygen pressure changes at various fractional conversions for Al-Mg 5% alloy ($T=700^\circ\text{C}$).

The points on figures 6a and 6b represent the ratios of the rates, in case of a sudden change in oxygen pressure ((a): Al-Mg 5%, from 400 to 200 hPa) or in temperature ((b) : Zircaloy-4, from 500°C to 530°C ($P_{\text{H}_2\text{O}} = 13 \text{ hPa}$, $P_{\text{H}_2} = 10 \text{ hPa}$)).



(a)



(b)

Figure 6: « $\Phi.E$ » test for Al-Mg 5% (a) (oxygen pressure changes from 400 to 200hPa (circles) and 200 to 400 hPa (squares)) and Zircaloy-4 (b) (temperature changes from 500 to 530°C).

For Al-Mg 5%, two domains of weight uptake can be distinguished in which the « $\Phi.E$ » test is verified : the rates ratio is approximately constant for a fractional conversion between 0 and 0.2 (weight uptake between 0.25% and 0.6%), and then between 0.3 and 0.52 (weight uptake between 1 and 1.7%), but the ratio value is different in each domain. This conclusion has been confirmed with isobaric experiments in which the temperature has been changed from 700 to 715°C. Besides, it has been verified that when the experiments are repeated several times at a given fractional conversion, the value of the rates ratio is nearly the same (error less than 10%). Thus, the growth reactivity Φ is reproducible, the non-reproducibility of the kinetic curves (figure 2) coming from the very irregular variations of the function $E(t)$. Moreover, it must be noticed that the magnesium activity a_{Mg} in the alloy varies during the oxidation reaction, so the fact that the « $\Phi.E$ » test is verified implies that the ratio of the rates does not depend on a_{Mg} in each domain of weight uptake : thus, either Φ is independent on a_{Mg} , or Φ can be written as the product of a function depending on a_{Mg} , $f(a_{Mg})$, and a function depending on P et T , $g(P, T)$, i.e. a_{Mg} is a separable variable in the expression of the growth rate.

For Zircaloy-4 (figure 6b), it can be observed that, considering the experimental error bars, the ratio of the rates keeps a constant value during the pre-transition stage (up to an oxide thickness of about 3 μ m). Then it decreases and takes lower values which remain between 1.16 and 1.38 during the post-transition domain, but the error bars do not overlap. Thus it can be concluded that the « $\Phi.E$ » test is only verified in the pre-transition domain, it is not verified in the post-transition stage since the ratio of the rates is not constant with the extent of weight increase, therefore the rate limiting step approximation is not valid.

Variations of Φ with the partial pressures P_i of the gases.

The experimental method to obtain the variations of Φ with P_i is also based on the sudden change method: in that case, several changes are carried out at a given weight gain, from a pressure P_0 to various pressures P (the temperature being constant). The ratio of the rates before and after the change, equal to $\frac{\Phi(P)}{\Phi(P_0)}$ according to [1], is proportional to the variations

of Φ with P , ($\Phi(P_0)$ keeping the same value in all the experiments).

For Al-Mg 5%, the variations of Φ with P_{O_2} were obtained by changing the oxygen pressure (from 200 to 800 hPa) at a fractional conversion 0.15 in the first domain of weight uptake ($\Delta m < 0.6\%$) and at 0.4 in the second domain of weight uptake ($1\% < \Delta m < 1.7\%$). Figure 7 shows that in each domain, Φ decreases strongly when the oxygen pressure increases, which is quite unusual for oxidation reactions.

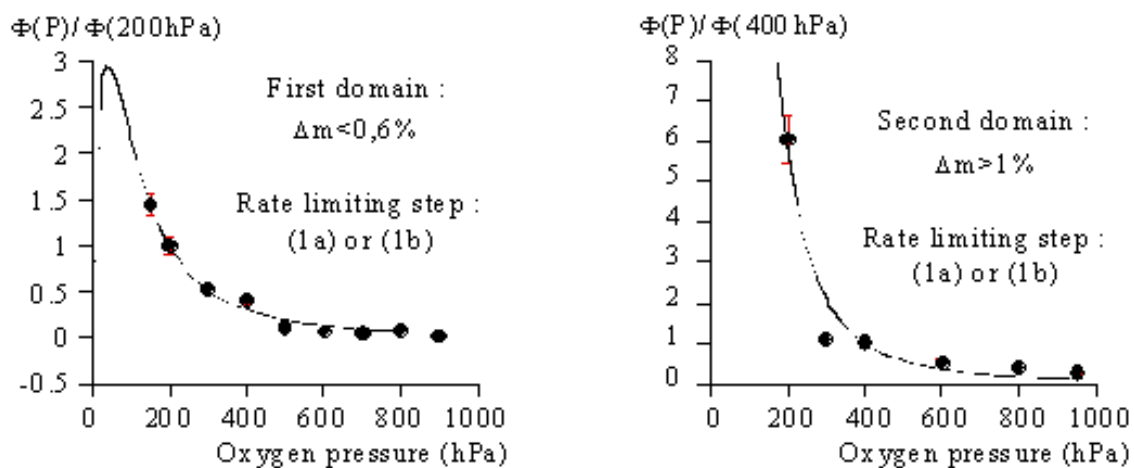


Figure 7: Variations of the growth reactivity Φ with the oxygen pressure in each domain of weight uptake, for Al-Mg5% alloy.

As it can be seen, the higher the oxygen pressure, the slower the rate, which justifies our choice of heating the samples under an oxygen pressure of one atmosphere before establishing the oxidation conditions at 700°C.

For Zircaloy-4, neither water vapour (change from 13 to 80 hPa) nor hydrogen (change from 10 to 40 hPa) have an influence on the oxidation rate in the pre-transition domain. On the contrary, after the transition, both gases have an accelerating effect on the rate of weight increase, as shown for example in figure 8 which gives the variations of $\frac{dm/dt(P)}{dm/dt(13\text{ hPa})}$ with $P_{\text{H}_2\text{O}}$, obtained by a series of sudden changes performed at various weight gains.

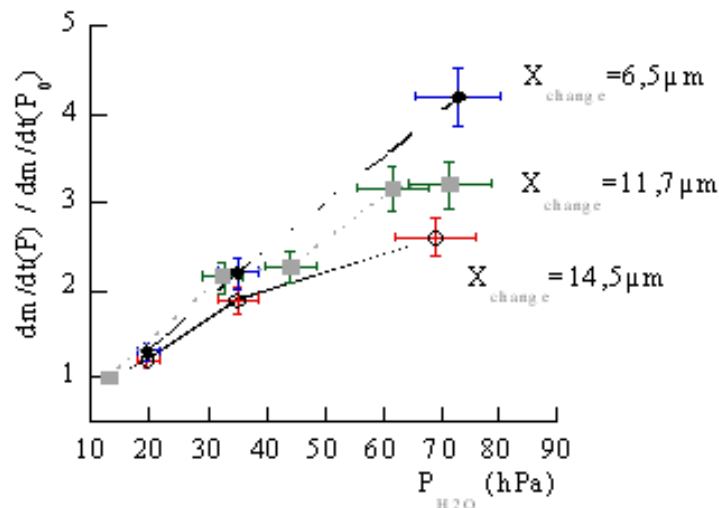


Figure 8: Ratios of weight increase rates before and after the pressure jumps at three equivalent thickness: $6.5\mu\text{m}$ (—), $11.7\mu\text{m}$ (◆) and $14.5\mu\text{m}$ (○) (530°C , $P_{\text{H}_2}=10\text{hPa}$).

GROWTH MECHANISMS

For the two reaction systems under study, we have verified experimentally that it will be possible to make the assumption of the rate-limiting step to calculate rate laws, using a growth mechanism involving elementary steps. Comparing these laws to the experimental variations of Φ with P_1 will normally lead us to determine the rate-limiting step of the reaction and thus the appropriate rate law for Φ .

In the case of Al-Mg 5%, the unusual variations of Φ with P_{O_2} could be accounted for by a growth mechanism involving two kinds of oxygen species adsorbed on the MgO surface. O_2^- species have been observed by IR spectroscopy (2, 20), and are found to be very stable. They are supposed to be inactive for the oxidation reaction and to occupy adsorption sites. A competitive and dissociative oxygen adsorption is assumed to occur on the same sites, leading to the adsorbed species involved in the oxidation process.

The steps proposed for the reaction mechanism are detailed in table II. A linear combination of the steps (1a), (1b), (2), (3) and (4) leads to the overall reaction: $\text{Mg} + \frac{1}{2} \text{O}_2 = \text{MgO}$. The rate laws have been calculated using the assumption of the rate-limiting step (2). Only the cases for which the steps of adsorption (1a), dissociation (1b) or external interface (2) are rate-limiting lead to rate laws which can account for a decreasing rate when the oxygen pressure increases (the same law is obtained in cases (1a) and (1b)).

Table II: MgO growth mechanism on Al-Mg 5% alloy

Non-dissociative adsorption (at equilibrium K_A)	$O_2 + s \Leftrightarrow O_{2-s}$
1) Dissociative adsorption in two steps	a) $O_2 + 4s \Leftrightarrow O_2$ b) $O_{2-s_4} \Leftrightarrow 2 O-s + 2s$
2) Creation of MgO defects (external interface)	$O-s \Leftrightarrow O_o + V_{Mg}'' + 2h^{\bullet} + s$
3) Diffusion of the defects from the external interface to the internal interface	
4) Internal interface reaction	$Mg_{alloy} + V_{Mg}'' + 2h^{\bullet} \Leftrightarrow Mg_{Mg_{oxide}}$

The function corresponding to the rate-limiting step (1a) or (1b) leads to a good agreement with the experimental values, the fitted curves are represented in figure 7. K_A (the equilibrium constant of the non-dissociative adsorption) is the only parameter to be adjusted, since in the ratios $\frac{\Phi(P)}{\Phi(P_0)}$ the rate constant (k_{1a} or k_{1b}) is eliminated. For the first and second domain of weight uptake, we obtain $K_A=7.9$ and $K_A=29$ respectively.

Thus, the existence of the two domains of weight uptake is linked to a change in the equilibrium constant K_A . Taking into account the two kinds of morphologies of magnesium oxide which have been observed (small grains and parallelepipeds), the two values of K_A may correspond to the oxygen adsorption on each oxide type. Thus, each domain of weight uptake can be attributed to a predominant morphology.

Concerning the rate limiting step, we can not conclude whether or not it is different from one domain to another (the rate laws (1a) and (1b) being the same).

In the case of Zircaloy-4, in the pre-transition stage, a simple growth mechanism for ZrO_2 can also be proposed, involving oxygen vacancies (4). Φ is independent on the water vapour and hydrogen partial pressures, zirconia growth can therefore be controlled by the diffusion of oxygen vacancies in the oxide layer. In that case, a parabolic law is expected for the curves giving the weight gain versus time (Wagner's model). But it is well known that the kinetic curves for zirconium alloys are rather cubic (10-12) ; to account for the deviation from the parabolic law, we have successfully tested the following equation (figure 9):

$$\frac{dX}{dt} = \frac{k_1}{X} \exp(-k_2 X) \quad [3]$$

in which k_1 and k_2 are constants which significance depends on the physical modelling (21-23), since at least two distinct assumptions may lead to this law : either the existence of barriers for the diffusing species (pores or cracks distributed at random inside the oxide layer (21, 22)), or the effect of a gradient of compressive stresses in the oxide layer (23). It has been suggested recently (24) that the cracks present in oxide scales grown on Zircaloy-4 in high water vapour pressure are probably obstacles for the diffusing species ; numerous short cracks being observed on our oxidised samples, it is in favour of the first assumption. Moreover, the coefficient k_2 of equation [3], which would in that case represent the number, per length unit, of barriers which cannot be passed through by the diffusing species, takes a value (from the numerical fitting) which is close to $1 \mu m^{-1}$. This value is acceptable considering the SEM observations (cf. figure 3a).

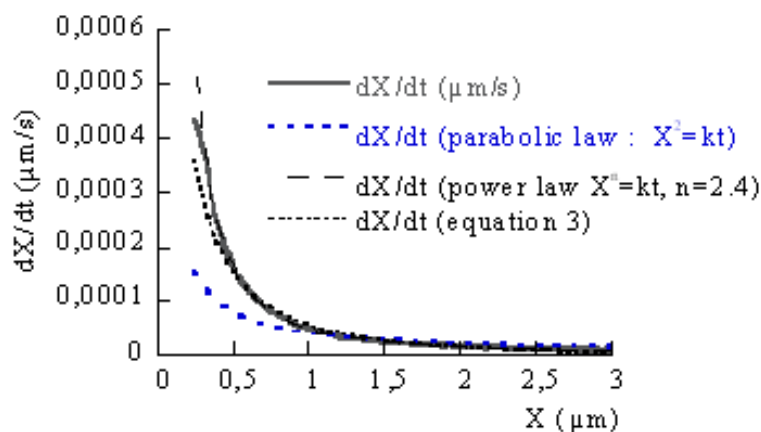


Figure 9: Rate of oxidation of Zircaloy-4 as a function of the oxide thickness before the kinetic transition – comparison with various rate laws.

In equation [3], the expression of the reactivity of growth Φ is exactly the same as in equation [2] (Wagner's theory for parabolic oxidation), contrarily to the expression of the function E , which is different due to the term $\exp(-k_2 X)$. Thus for a given thickness X , E is smaller than in Wagner's model (in that case, $k_1 = V_{ox} D_v \Delta C_v$, where V_{ox} is the molar volume of the oxide).

Concerning the kinetic transition, it is clear from the results of the sudden change method (cf figure 6b) that the rate limiting step controlling the beginning of the oxidation is no longer valid even before the rate has reached its minimal value. The degradation of the oxide layer associated to the perpendicular cracks connected to the gaseous atmosphere is observed on samples oxidised up to after the transition. It is interesting to note that the previous explanations of the kinetic transition (a sequence of quasi parabolic diffusion-controlled periods, or a rate limiting step of diffusion in a dense layer of constant thickness close to the metal/oxide interface) are in contradiction with the « $\Phi.E$ » test results, since in both cases, the « $\Phi.E$ » test would have been verified (constant ratios). It appears that a new mechanism must be considered, taking into account the partial pressure effects and the appearance of a porous layer which contains the cracks perpendicular to the surface.

CONCLUSIONS

A new approach to the investigation of reaction mechanisms in solid state reactions has been proposed, based on the study of the oxidation kinetics of two alloys.

In the case of Al-Mg 5% alloy, the use of the P or T jumps method turned out to be necessary to overcome problems due to the non-reproducibility of the kinetic curves, and to obtain the variations of Φ with P_{O_2} . It has been shown that Φ decreases when oxygen pressure increases, which was accounted for by a mechanism involving two parallel oxygen adsorptions. Moreover, evidence for two domains of weight uptake has been found, in which the growth rate Φ is different, although the rate-limiting step seems to be the same. The origin of these two domains could not be identified with certainty, but SEM observations showing that the oxide exists in two different morphologies, and the suggested mechanism leading to distinct values of the equilibrium constant of oxygen adsorption K_A in the two domains of weight uptake, each domain could correspond to a predominant oxide morphology.

In the case of Zircaloy-4, this method allowed to point out clear differences between the pre- and post transition stages of oxidation: in pre-transition, the oxidation is controlled by a rate-limiting step, most probably the diffusion of oxygen vacancies through the oxide layer. This is no longer the case after the transition, moreover water vapour and hydrogen have an accelerating effect on the oxidation rate (whereas they have no effect in pre-transition). These

results can be explained by a change in the reaction mechanism, probably related to the changes in the porous structure of the oxide layer.

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