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Determination of Parabolic Rate Constants from a Local Analysis of Mass-Gain Curves

Daniel Monceau* and Bernard Pieraggi*

A method is proposed to allow a more accurate evaluation of thermogravimetric data to identify diffusion or partial diffusion control of scaling kinetics. This method is based on the fitting of mass-gain data to a parabola over a short time interval. The translation of the time interval over the entire test time period provides an actual instantaneous parabolic rate constant independently of any transient stage or simultaneous reaction steps. The usefulness and limitations of this procedure are illustrated from oxidation tests performed on several metallic materials (pure nickel, single-crystal superalloys, and Nb-Ti-Al alloy).

KEY WORDS: data analysis; thermogravimetry; growth kinetics; parabolic rate constant.

INTRODUCTION

One step in studying the high-temperature oxidation or corrosion of any kind of material is to determine its overall oxidation kinetics. Oxidation kinetics are commonly controlled by the diffusion of reactive species through the external oxide scale and/ or in the subjacent metal or alloy.^{1,2} Diffusion-driven oxidation kinetics usually lead to the so-called parabolic kinetics that are commonly described through a parabolic rate constant, k_p . However, the definition of an instantaneous k_p , and its variation with time, has been considered by several authors (e.g., refs. 3– 5) to explain apparent discrepancies occurring between observed experimental and purely parabolic growth kinetics. Such discrepancies are often observed for relatively

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short-term exposures for which many factors may affect scaling kinetics. Some of these factors, such as the variation of diffusion coefficients within the scale as a function of oxide grain size or scale compositions are inherent to the growing scale, but heating procedure, surface preparation, and specimen handling are also known to drastically influence the first stage of scale growth. For example, these factors are of great importance for the oxidation of alloys for which a transient stage often occurs before the steady-state growth of a continuous scale of the most stable oxide (for example, transformations of metastable forms of alumina into the stable α -alumina, or a change of the alloy composition below the oxide scale). Furthermore, the interfacial-reaction steps associated with mass or defect transfer at the gas-scale and/or scale-alloy interfaces may, at least partially, contribute to the control of scale growth,⁶⁻⁸ so that the growth kinetics are described by at least two rate constants, k_p and k_l , as will be seen below. Therefore, ignoring the role of interface reactions and the associated linear rate constant k_l may lead to an apparent parabolic constant k_p^{app} [e.g., defined as some local slope of the thermal gravimetric analysis (TGA) data] that varies with time. Thus, any method permitting a more accurate analysis of experimental data would be useful in providing more reliable interpretations of these data.

TGA permits continuous and accurate measurements over long periods of time and, therefore, an accurate determination of oxidation kinetics in their integral form or derivative form. Furthermore, the increasing storage and calculation capacity of computers allows one to take advantage of the improving performances of automatic-recording thermobalances in terms of accuracy, sensitivity and reproducibility. Fast personal computers now permit a careful systematic analysis of a continuous mass-gain recording. A method to quantitatively evaluate the time evolution of actual instantaneous parabolic rate constants is proposed in the present work. The method is illustrated by its application to several sets of experimental data corresponding to commonly encountered oxidation behavior for pure metals or alloys.

ANALYSIS OF SCALING KINETICS

Rate Equations and Kinetic Laws for Metal and Alloy Oxidation

Since the classic works of Tammann⁹ and Pilling and Bedworth,¹⁰ the oxidation kinetics of metals and alloys determined from thermogravimetry are commonly described through a parabolic law

$$\Delta m^2 = k_p t$$

where Δm is the mass gain per unit area at time t and k_p is the parabolic rate constant. The Wagner theory of metal oxidation has shown that such

parabolic kinetics result from the control of scale growth by lattice or volume diffusion so that k_p is then related to the self-diffusion coefficients of cations or anions across the scale.¹¹ However, this purely parabolic law satisfactorily applies to the oxidation kinetics at high temperature of only a limited number of pure metals. Deviations are often observed and reported in the literature for the oxidation of pure metals (e.g., for pure nickel^{3-5,12-14}) or alloys (e.g., refs. 15 and 16), particularly at intermediate temperatures, i.e., at temperatures lower than about $0.5 T_m$ (K), where T_m is the melting temperature of the growing oxide.

Independent of any changes in scale-growth mechanisms, which might depend on time and/or temperature, a common misinterpretation in the use of equation " $\Delta m^2 = k_p t$ " results from overlooking the initial condition required to integrate the rate equation. Indeed, the integration of the common rate equation

$$\frac{d\Delta m}{dt} = \frac{k_p}{2\Delta m} \quad (1a)$$

is achieved through the initial condition " $\Delta m = 0$ at $t = 0$ and constant temperature," a condition that is quite difficult to achieve experimentally. For example, before the test temperature is reached and stabilized, test specimens can be oxidized during the initial heating period. Even in the case of specimen heating in a nonoxidizing or reducing atmosphere, which is not always possible, the introduction of oxidizing gas often disturbs the temperature and measurement of mass changes for several minutes and leads to a systematic error for the starting point of mass-gain curves.

The above equations are also used to describe the oxidation kinetics of alloys. The most commonly encountered difficulty is then the occurrence of a transient-oxidation period when the oxidation of more-noble components occurs simultaneously with the oxidation of the less-noble and more-protective component (e.g., chromia- or alumina-former alloys).^{15,16}

Transient oxidation is also observed during the initial stages of oxidation of pure metals. In this case, the initially fast reaction rates may be related to local thermal instabilities (heat release), to the fast nucleation kinetics of oxide grains leading to microstructural instabilities, or to the very high gradient in chemical potential through the thin initial oxide scale. Thus, usually the initial condition $\Delta m = 0$ at $t = 0$ cannot be applied. To account for the transient oxidation period of nonparabolic kinetics, the initial condition could be $\Delta m = \Delta m_i$ at $t = t_i$; the integration of Eq. (1a) then leads to

$$\Delta m^2 - \Delta m_i^2 = k_p (t - t_i) \quad (1b)$$

by assuming that the oxide scale grown at $t > t_i$ has the same protective properties as the initial scale grown at $t < t_i$. For example, Eq. (1b) applies to the growth kinetics of alumina scales on NiAl¹⁷ characterized by the growth of less-protective metastable aluminas and their subsequent transformations into a protective scale of α -alumina. However, if the initial oxide scale is not protective or much less protective than the stable oxide scale growing at $t > t_i$, then the following rate equation

$$\frac{d\Delta m}{dt} = \frac{k_p}{2(\Delta m - \Delta m_i)} \quad (2)$$

is more appropriate than the “classic” Eq. (2).^{14,18,19} In Eq. (2), Δm_i is the initial mass change before the establishment of the kinetic regime associated with the parabolic growth of the stable oxide scale.

The preceding Eqs. (1a) to (2) suppose that the oxidation kinetics are solely controlled by diffusion inside the scale, i.e., the hypothesis is made that diffusion of the reactive species within the scale is the rate-limiting step in the overall oxidation process. However, if among the several series reaction steps associated with the formation and growth of an oxide scale, one linear interfacial step is sufficiently slow to not be neglected, then the overall diffusion and reaction process is described by the following rate equations:⁶⁻⁸

$$\frac{d\Delta m}{dt} = \frac{1}{(1/k_i) + (2\Delta m/k_p)} \quad (3)$$

or

$$\frac{d\Delta m}{dt} = \frac{1}{(1/k_i) + (2(\Delta m - \Delta m_i)/k_p)} \quad (4)$$

where k_p and k_i are the rate constants for the pure diffusion and pure reaction steps, respectively. As shown by the rate equations and kinetic laws listed in Table I, upon integration, these rate equations lead to kinetics laws which depend on the initial conditions and on the protective or unprotective character of the scale formed during the transient oxidation.

Equations (2) and (4) are particularly adapted to describe the kinetics of the selective oxidation of an alloy that is commonly preceded by an initial fast-oxidation regime corresponding to the growth of less-protective oxide (e.g., refs. 15 and 16).

It should be noted here that it is meaningless to give a value of k_p in time ranges where the coefficient C is not constant. All the rate equations reported in Table I, and their analytical solutions (kinetics laws of Table I),

Table I. Common Rate Equations and Kinetics Laws for Metal or Alloy Oxidation

Case	Rate equation	Initial conditions	Kinetics law
1	$\frac{d\Delta m}{dt} = \frac{k_p}{2\Delta m}$	$t = t_i$ $\Delta m = \Delta m_i$ Same first oxide	$\Delta m^2 - \Delta m_i^2 = k_p(t - t_i)$
2	$\frac{d\Delta m}{dt} = \frac{k_p}{2(\Delta m - \Delta m_i)}$	$t = t_i$ $\Delta m = \Delta m_i$ Unprotective first oxide	$(\Delta m - \Delta m_i)^2 = k_p(t - t_i)$
3	$\frac{d\Delta m}{dt} = \frac{1}{(1/k_i) + (2\Delta m/k_p)}$	$t = t_i$ $\Delta m = \Delta m_i$ Protective first oxide	$t - t_i = \frac{\Delta m^2 - \Delta m_i^2}{k_p} + \frac{(\Delta m - \Delta m_i)}{k_i}$
4	$\frac{d\Delta m}{dt} = \frac{1}{(1/k_i) + (2(\Delta m - \Delta m_i)/k_p)}$	$t = t_i$ $\Delta m = \Delta m_i$ Unprotective first oxide	$t - t_i = \frac{(\Delta m - \Delta m_i)^2}{k_p} + \frac{(\Delta m - \Delta m_i)}{k_i}$

are valid for constant values of k_p and k_i : the rate equation and its integration would be different if k_p and k_i must be considered to vary with time.

Apparent and True Parabolic Rate Constants

The fitting of any thermogravimetric data to equation “ $\Delta m^2 = k_p t$ ” leads implicitly to an apparent instantaneous parabolic rate constant k_p^{app} in place of the pure parabolic rate constant k_p considered in Eqs. (1–4) (a correct determination of the pure k_p is explained later). At a given time t , k_p^{app} could then be considered to be the slope of the $(\Delta m^2, t)$ curve, i.e., the quantity $2\Delta m(d\Delta m/dt)$, which is sometimes interpreted to describe the time evolution of the parabolic rate constant (e.g., refs. 3–5, 12, and 13). As shown by the expression of the ratio between k_p^{app} and k_p reported in Table II, the apparent rate constant, k_p^{app} , can differ significantly from the real

Table II. k_p^{app} to k_p Ratio for the Cases Considered (see Table I) of Oxidation Processes

Case	Rate equation	k_p/k_p^{app}
1	$\frac{d\Delta m}{dt} = \frac{k_p}{2\Delta m}$	$\frac{k_p}{k_p^{\text{app}}} = 1$
2	$\frac{d\Delta m}{dt} = \frac{k_p}{2(\Delta m - \Delta m_i)}$	$\frac{k_p}{k_p^{\text{app}}} = 1 - \frac{\Delta m_i}{\Delta m}$
3	$\frac{d\Delta m}{dt} = \frac{1}{(1/k_i) + (2\Delta m/k_p)}$	$\frac{k_p}{k_p^{\text{app}}} = 1 + \frac{k_p}{2\Delta m k_i}$
4	$\frac{d\Delta m}{dt} = \frac{1}{(1/k_i) + 2(\Delta m - \Delta m_i)/k_p}$	$\frac{k_p}{k_p^{\text{app}}} = 1 + \frac{k_p}{2\Delta m k_i} - \frac{\Delta m_i}{\Delta m}$

Table III. Correspondence Between Parabolic Coefficients (A, B, C) and Kinetics Parameters (k_p, k_l)

Case	Kinetic law	A	B	C
1	$\frac{\Delta m^2 - \Delta m_i^2}{k_p} = t - t_i$	$t_i - \frac{\Delta m_i^2}{k_p}$	0	$\frac{1}{k_p}$
2	$\frac{(\Delta m - \Delta m_i)^2}{k_p} = t - t_i$	$t_i + \frac{\Delta m_i^2}{k_p}$	$-\frac{2\Delta m_i}{k_p}$	$\frac{1}{k_p}$
3	$t - t_i = \frac{\Delta m^2 - \Delta m_i^2}{k_p} + \frac{(\Delta m - \Delta m_i)}{k_l}$	$t_i - \frac{\Delta m_i}{k_l} - \frac{\Delta m_i^2}{k_p}$	$\frac{1}{k_l}$	$\frac{1}{k_p}$
4	$t - t_i = \frac{(\Delta m - \Delta m_i)^2}{k_p} + \frac{(\Delta m - \Delta m_i)}{k_l}$	$t_i - \frac{\Delta m_i}{k_l} + \frac{\Delta m_i^2}{k_p}$	$\frac{1}{k_l} + \frac{2\Delta m_i}{k_p}$	$\frac{1}{k_p}$

rate constant, k_p . Moreover, the time evolution of k_p^{app} does not necessarily involve a change in the oxide-scale properties, but can be explained by only the occurrence of a short transient-oxidation period and/or slow reaction steps. This time evolution depends mainly on the amplitude of the transient mass gain Δm_i and of the linear rate constant k_l .

Therefore, rather than the determination of k_p^{app} , the analysis of thermogravimetric data must provide an accurate determination of the true parabolic rate constant k_p , which is the only parameter strictly related to the diffusion processes involved in the oxidation mechanisms. Then, if a time evolution of k_p is observed over a long time period, then a more detailed analysis of the data would be required to relate the evolution of this rate constant to a change in the growth mechanisms or a change in the diffusion constant during the course of oxidation.

Analysis of Experimental Data and Adjustment Procedure

As shown by the kinetics laws listed in Table I, all the considered kinetics correspond to a variation of mass gain vs. time, which can be fitted to a parabola

$$t = A + B \Delta m + C \Delta m^2 \quad (5)$$

Table III shows which kinetics parameters can be evaluated from the coefficients A , B , and C obtained from such a fit. The most important feature is that the second degree coefficient C is always the reciprocal of the “true” parabolic rate constant. *The fitting of the experimental data to a complete parabola permits a correct evaluation of k_p independently of the effective oxidation mechanism and/or the occurrence of transient oxidation.* Moreover, k_p does not depend on the values of Δm_i and t_i , which fix the

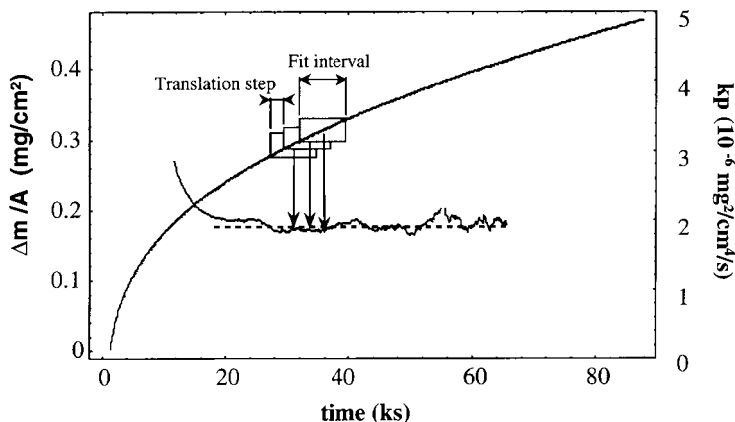


Fig. 1. Illustration of the "local parabolic fitting" algorithm. The time-window is translated over the entire data set.

initial condition for integrating the rate law. On the contrary, the coefficients B and A would permit the determination of k_l and of the characteristic elements Δm_i and t_i of the transient period for only some specific cases. In the most general case that a reaction step and diffusion jointly control throughout a transient period k_l , Δm_i , and t_i cannot be evaluated. However, as the fit to Eq. (5) covers all the cases considered, taking care of both a transient stage and an interfacial reaction, it would always be better to fit the experimental data to Eq. (5) rather than to " $\Delta m^2 = k_p t$."

The fit of experimental data to a general parabola can be applied to the entire set of data or only to a portion thereof, corresponding to a given time interval. When using such local calculations, any evolution or change of the parabolic rate constant as a function of time can be detected. Therefore, a numerical method was developed to calculate, for a short time interval, the parabolic constant from the least-squares fit of $(\Delta m, t)$ data to a parabola. This local fit allows one to determine the value of the parabolic rate constant for the time interval considered. The repetition of this time interval calculation over the entire test time period permits one to detect and analyze any change or evolution of the parabolic rate "constant" as a function of time.

This "local parabolic fitting" procedure is illustrated on Fig. 1 and detailed in the Appendix. The accuracy of the analysis depends on three factors: (1) Accurate mass gains must be recorded as a function of time and the maximum number of $(\Delta m, t)$ couples, which can be stored by the equipment, should be used. (2) The size of the time window is decided by a compromise between two opposing objectives: reduction of noise and

increase in time resolution, which corresponds typically to a smoothing procedure. In case of large mass gains, the size of the time window can be reduced, leading to a better time resolution. (3) Choose the translation step of the time window. This is just a question of time resolution vs. computing time, which nowadays, is not a problem for such a simple algorithm.

EXAMPLES OF DATA ANALYSIS

To illustrate the advantage of this procedure, it was tested on data for the oxidation behavior of several materials studied in our laboratory. These tests demonstrated the usefulness and accuracy of this procedure and it is now currently used routinely for analyzing thermogravimetric data.

All the data reported in the following examples were obtained from oxidation tests performed on an automatic recording thermobalance SETARAM TAG 24S equipped with a double symmetrical furnace that permits a compensation for any perturbation resulting from gas flow, buoyancy, and convection. This symmetrical furnace provides a very stable signal and minimizes the drift error to less than $3 \mu\text{g}$ for a test duration of 24 hr. Each test record was limited in size to 4000 ($\Delta m, t$) couples and the parameters of local fitting were calculated for a time interval containing 200 ($\Delta m, t$) couples.

Oxidation of Pure Nickel

The time evolution of an instantaneous, apparent parabolic rate constant has been reported for the oxidation kinetics of pure nickel.^{3-5, 12-14} In a study of the effect of superficial alkaline-earth doping on the oxidation of nickel, the oxidation kinetics of high-purity nickel were again determined for tests performed in pure oxygen at temperatures between 600 and 1200°C for 24 hr.²⁰ The local fit procedure was applied with a translation step of the time interval of 22 s between 20 min and 24 hr. Figure 2a shows the oxidation kinetics at 600°C; Fig. 2b shows the variation as a function of time of k_p^{app} (calculated according to $2\Delta m(d\Delta m/dt)$) and also of $k_p=C^{-1}$. Figure 2b shows that k_p remains practically constant as soon as the time exceeds about 3 hr, while k_p^{app} varies over a much longer time period and is always greater than k_p . For one time interval extending from 15 to 90 ks, the experimental mass-gain curve can be fitted to a single parabola (Fig. 2a) corresponding to a constant k_p equal to $1.9 \times 10^{-6} \text{ mg}^2 \text{ cm}^{-4} \text{ s}^{-1}$. Figure 2b shows that this value of k_p corresponds exactly to the mean value calculated from the local fitting procedure. Therefore, at test times exceeding 4 hr, the growth kinetics can be described by a classic parabolic law, but it is preceded by a transient regime of faster kinetics. Figures 2a and b clearly illustrate that the difference between the apparent (k_p^{app}) and "true" (k_p)

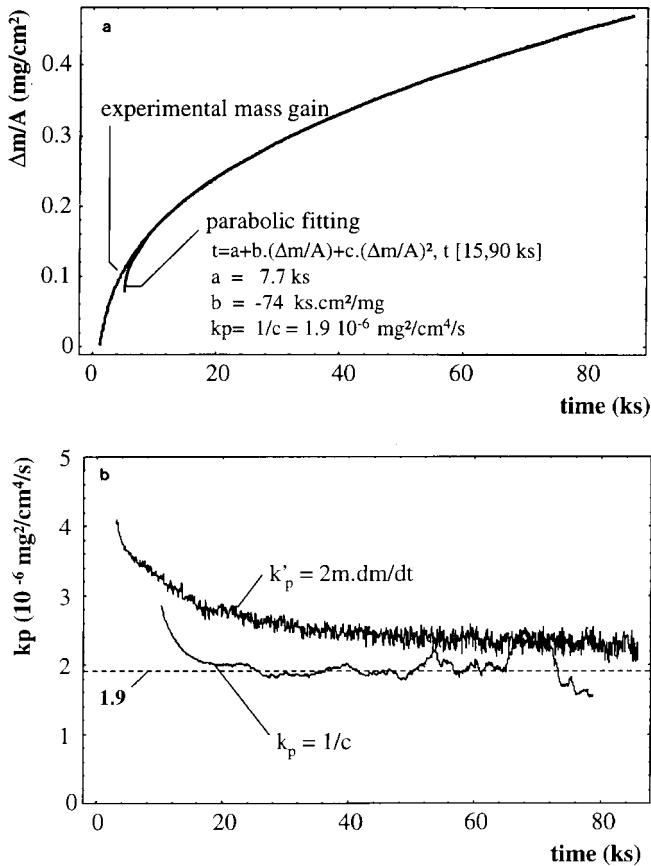


Fig. 2. Oxidation kinetics for pure nickel at 600°C in oxygen.²⁰ (a) Mass gain vs. time and parabolic fitting between 15 and 90 ks; (b) comparison of k_p^{app} and k_p calculated from the local fitting procedure.

constants is the consequence of the extra mass gain associated with the fast transient period. Thus, the local fitting procedure permits one to accurately calculate k_p independent of any change in growth kinetics.

To better illustrate the potential and the advantage of this fitting technique, an experiment was done to determine the parabolic rate constant, k_p , at several temperatures from one single thermogravimetric test. From the data reported by Gonzalez-Balanchi²⁰ for the oxidation of pure nickel, a temperature program was applied to one test specimen. It consisted of a succession of isothermal periods whose durations were selected to lead to approximately the same mass gain of 1 mg cm $^{-2}$. Figure 3 shows the temperature program and the corresponding mass-gain curve. As illustrated by

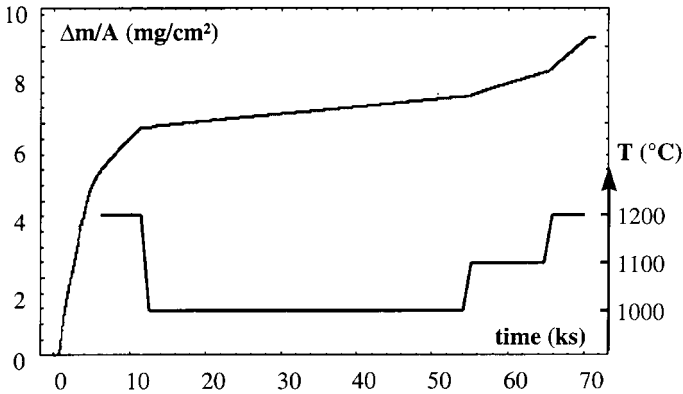


Fig. 3. Temperature program applied to a pure-nickel specimen oxidized under oxygen at atmospheric pressure and corresponding mass-gain curve.

Fig. 4, each isothermal period of the mass-gain curve can be fitted to only one parabola. Comparison of Fig. 4a and d shows that the reproducibility is excellent. Moreover, as shown from Table IV, the rate constants k_p determined in this way are in good agreement (a factor 3 or less) with those obtained from entirely isothermal experiments despite the small mass gains. No other calculation procedure would have permitted such an accurate measurement of the individual rate constants for each isothermal period; linear regression from $(\Delta m^2, t)$ data or even $(\Delta m, t^{1/2})$ would not lead to such an accurate value of k_p .

Oxidation of Single-Crystal Ni-Base Superalloy

A more obvious and important examination of the transient-oxidation regime is encountered during the oxidation of alumina-forming alloys. For example, Ni-base superalloys form an alumina scale when oxidized above 1000°C, but the growth of a Ni-rich oxide, spinel phases, and transition aluminas may occur during the heating period and before completion of a continuous protective α -alumina scale. The fast growth of these transient oxides during the first 2-hr leads to a mass gain at least of the magnitude for the mass gain by alumina growth during 24 hr.²¹ A direct consequence of these initially fast oxidation kinetics is once again that the Δm^2 vs. t fit (or $k_p^{\text{app}} = 2\Delta m(d\Delta m/dt)$) would require very long experiments before ever reaching the “true” k_p value characteristic of alumina growth (Fig. 5a and b).¹⁶ This example illustrates one limit of the proposed local fitting procedure: Fig. 5b shows that the width of the scatter band for k_p increases with time. Indeed, the ratio between the mass gain during the considered

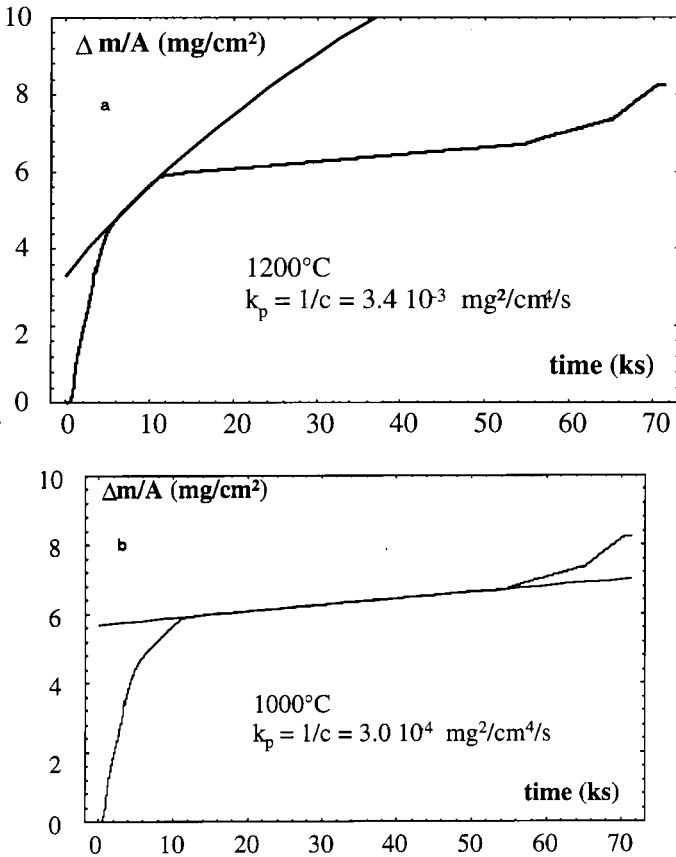


Fig. 4. Nickel oxidation: fitting of successive portions of the mass gain vs. time plot. (a) 1200°C ; (b) 1000°C ; (c) 1100°C ; (d) 1200°C .

time interval and the experimental mass-gain sensitivity, i.e., the signal-to-noise ratio, decreases over time. This effect is particularly important for a slow-growing oxide, such as alumina. However, even if it would be possible to maintain a signal-to-noise ratio approximately constant by increasing the time interval, the gain in accuracy would not be significant compared to other possible error sources. Checking the constancy of k_p over a large part of the test time is more important and significant than a very accurate measurement of k_p , whose value is strongly dependent on surface preparation, local composition and heterogeneity, gas composition, etc.

Oxidation Kinetics of Nb-Ti-Al Alloy

This last experimental example concerns the oxidation of a Nb-Ti-Al alloy. The accuracy of mass-change measurements and the signal stability

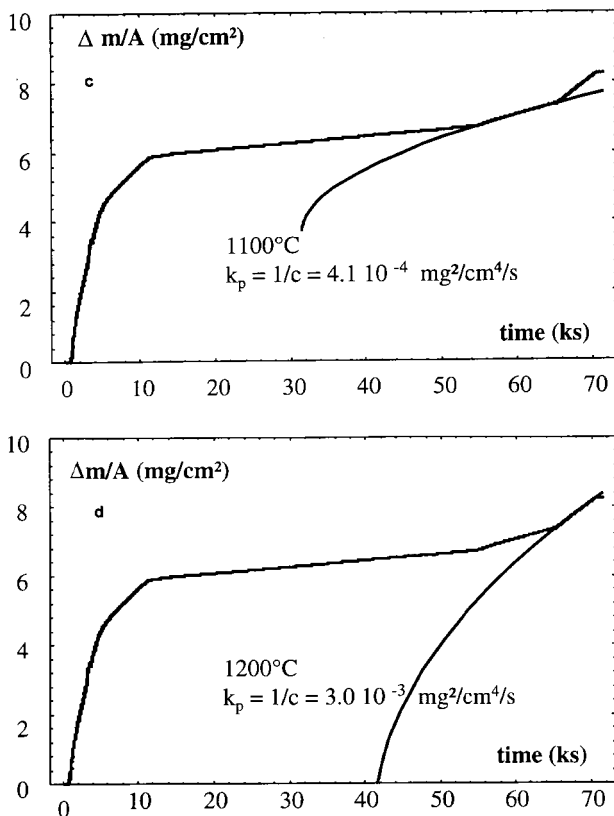


Fig. 4. Continued.

permitted the detection of a small irregularity in mass-change curves as shown in Fig. 6a.²¹ Indeed, the mass gain vs. time plot clearly shows several local changes of slope indicative of a succession of protective-scale growth and scale failures (Fig. 6a). The local fitting procedure is well adapted to analyze these complex kinetics. First, this procedure allows one to localize

Table IV. Parabolic Rate Constants k_p Determined from Local Fit from Nonisothermal and Isothermal Tests

T (°C)	Holding time (hr)	k_p (local fit) ($\text{mg}^2 \text{cm}^{-4} \text{s}^{-1}$)	k_p (24-hr isothermal test) ($\text{mg}^2 \text{cm}^{-4} \text{s}^{-1}$)
1200	2.8	3.4×10^{-3}	7.4×10^{-3}
1000	12	3.0×10^{-4}	3.3×10^{-4}
1100	2.8	4.1×10^{-4}	1.3×10^{-2}
1200	1.5	3.0×10^{-3}	7.4×10^{-3}

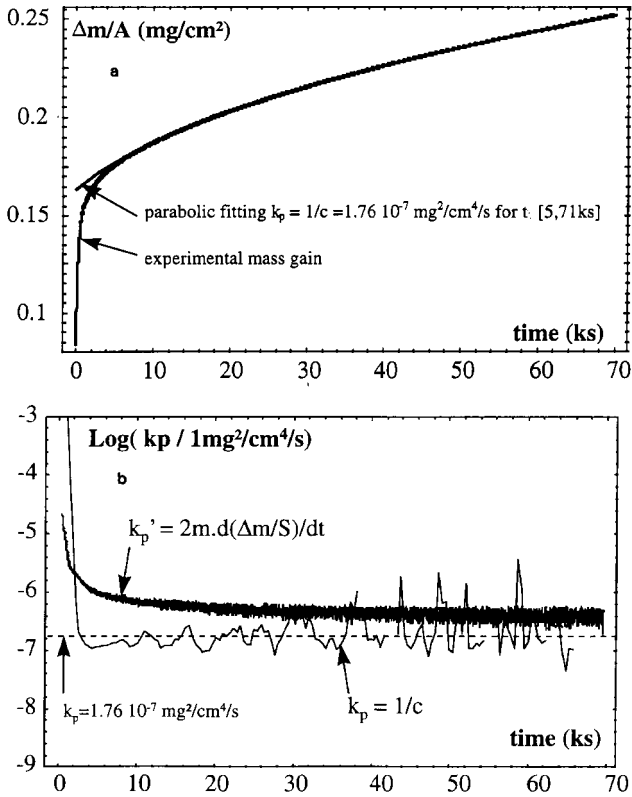


Fig. 5. Oxidation kinetics for a Ni-base superalloy at 1100°C in oxygen. (a) Mass gain vs. time plot²¹ and parabolic fitting between 5 and 71 ks; (b) comparison of k_p^{app} and k_p calculated from the local parabolic-fitting technique.

clearly the time periods of parabolic kinetics. Indeed, the coefficient C is null at inflection points, which corresponds to an infinite local $k_p = C^{-1}$ between each parabolic period. Second, Fig. 6b shows that the minimum values of local k_p are approximately equal within each period. These minimum values ($k_p = 6.0 \cdot 10^{-3} \text{ mg}^2 \text{ cm}^{-4} \text{ s}^{-1}$) are quite different from the value that approximately fits the experimental curve to a single parabola over the entire plot ($k_p = 1.5 \cdot 10^{-2} \text{ mg}^2 \text{ cm}^{-4} \text{ s}^{-1}$). These minimum k_p values are more than a factor two smaller than the minimum apparent rate constants calculated from $2\Delta m(d\Delta m/dt)$. Moreover, there is no time coincidence between the minimum in k_p^{app} and k_p . This large discrepancy between the two analyses can be attributed to the overestimation by k_p^{app} , which is intrinsic in its calculation. Indeed, the value of Δm entering into this calculation is not the

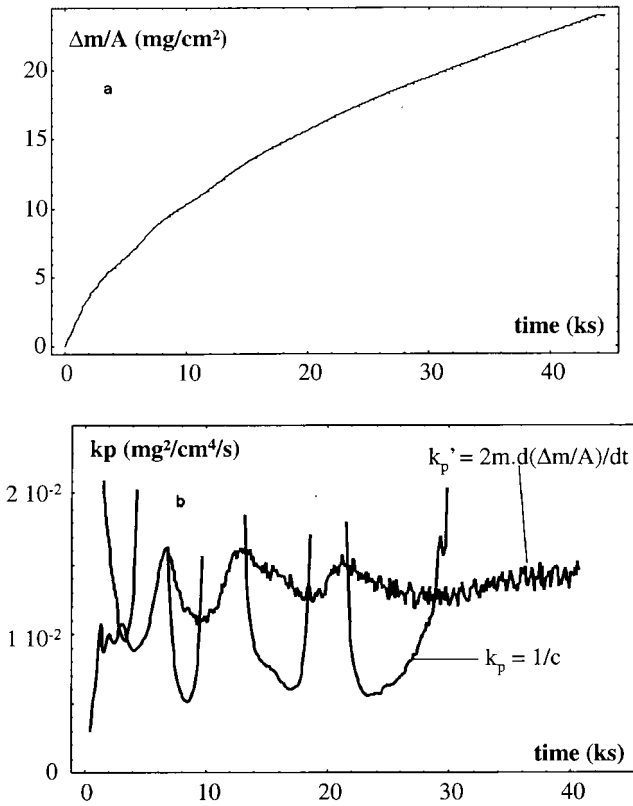


Fig. 6. Oxidation kinetics of one Nb-Ti-Al alloy at 900°C in air. (a) Mass gain vs. time plot;²² (b) Comparison of k_p^{pp} and k_p calculated from the local parabolic-fitting technique.

value that must be considered in the rate equation. The local fitting is, therefore, much more appropriate and leads to k_p values that permit a more accurate analysis of the scale-growth kinetics during the growth of the temporary protective scale, because this procedure leads to the correct value independent of the origin chosen for the calculation (cf. Table III).

CONCLUSIONS

The above analyses of experimental data for scale-growth kinetics show that the use of the classic " $\Delta m^2 = k_p t$ " fit (i.e., the Δm^2 vs. t plot) should be systematically replaced by the more general procedure of fitting to a complete parabola " $t = A + B \Delta m + C \Delta m^2$." The use of classic " $\Delta m^2 = k_p t$ " fit

involves unnecessary assumptions (e.g., pure diffusion control and no transient regime), which may lead to a misinterpretation of kinetics and to apparent variations in rate constants, i.e., of diffusion properties for oxides. The complete parabolic fit offers the advantage of accounting for pure diffusion control, mixed (diffusion/reaction) control, and a transient regime. Furthermore, it can be applied to small portions of mass-gain curves, which then allows the calculation of an instantaneous value of the parabolic “constant” $k_p=C^{-1}$ inherently better than the usual $k_p=2\Delta m(d\Delta m/dt)$.

To interpret experimental mass-gain data, the following systematic procedure can be proposed. First, the kinetics data should be fitted to the Eq. (5) inside a time-window sliding over the entire experiment duration (Fig. 1). This first test allows the determination of those time periods over which the oxidation kinetics are parabolic. Second, data can be fitted to Eq. (5) over the entire time range, where the fitting coefficient “ C ” (Eq. (5)) appears to be constant in the first test. This allows one to accurately compute the value of the local true parabolic rate constant $k_p=C^{-1}$ inside these specific time ranges. The values of the fitting coefficients “ A ” and “ B ” (Eq. (5)) can provide insight about the relative importance of the linear and parabolic rate constants, but the value of the constant k_l cannot be calculated in the most general cases considered here (cases 3 and 4, Tables I and III), since the rate equations involve four unknown parameters and the parabolic fitting permits one to determine only three coefficients. Additional assumptions are then needed in order to simplify the kinetics model.

APPENDIX. NUMERICAL PROCEDURE TO ANALYZE THE THERMOGRAVIMETRIC DATA (MASS GAIN AS A FUNCTION OF TIME)*

Experimental mass gain file name (s, mg/cm²) corresponding to Fig. 2

```
title="nid912.txt";
```

Read the experimental file and build the mass vs. time list:

```
time_mass=ReadList[title,Number,RecordLists->True];
```

Build a new table: time as a function of mass in order to perform the parabolic fit

```
time_as_a_function_of_mass=Table[Reverse[time_mass[[i]],i,1,Length[time_mass]]];
```

*This example was written with Mathematica® version 3.0.

This sequence performs the local full parabolic fitting:

```
deltai=100; (size of the sliding window in which the fit is performed, in number of points)
kp_list=0,0;

Do[ imin=i;
    imax=imin+deltai;
    time_window=Take[time_as_a_function_of_mass,imin,imax];
    polyfit=Fit[time_window,1,x,x^2,x];
    kp=1/Coefficient[polyfit,x,2];
    kp-list=Append[kp_list,time_mass[[Ceiling[(imin+imax)/2]]][[1]],Log[10,kp]]
    ,i,1,Length[time_mass]-deltai,step];
```

Plot the result: k_p as a function of time (see Fig. 2b)

```
plotkp=ListPlot[kp_list,PlotStyle→RGBColor[1,0,0],PlotRange→{kpmin,kpmax}]
```

From the last result, select the largest time-window where the k_p is constant in order to get a precise value of the true parabolic constant k_p (here, between 15 and 80 ks).

```
time_min=15000;      time_max=80000;
imin=1;             imax=Length[time_mass];
While[time_as_a_function_of_mass[[imin]][[2]]<timemin,imin=imin+1];
While[time_as_a_function_of_mass[[imax]][[2]]>time_max,imax=imax-1];
time_window=Take[time_as_a_function_of_mass,imin,imax];
polyfit=Fit[time_window,1,x,x^2,x];
A=Coefficient[polyfit,x,0];
B=Coefficient[polyfit,x,1];
kp=1/Coefficient[polyfit,x,2];
mass_fit=kp*(Sqrt[b*b-4*(a-x)/kp]-b)/2
plotdufit=
Plot[mass_fit,x,0,time_mass[[Length[time_mass]]][[1]],PlotStyle→RGBColor[1,0,0]];
Print["kp calculated between=",time_min," s and t=",time_max," s, "kp=", kp]
```

The resulting plot and k_p , A , and B values are given in Fig. 2a.

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