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Numerical study of the influence of the total mass of oxide formed during heating on the parabolic kinetic constant kp characterizing the high temperature oxidation rate of chromia-forming alloys

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ABSTRACT

Thermogravimetry is a very useful technique for accessing the kinetic description of the high temperature oxidation progress. Classical methods for deducing the value of k_p, the kinetic constant characterizing the parabolic oxidation in isothermal condition may lead sometimes to underestimated values, often minimizing the real oxidation rate. Here, exploiting some real experimental data, a mathematical study of the kinetic of oxidation during heating and of the dependence of the total mass gain achieved at heating on the heating rate and the mass variation recoding step, was preliminarily realized. The values obtained for this mass gain during heating in stabilized conditions were thereafter used to study the consequences of this first oxidation on the classically determined k_p values. In parallel another type of determination was applied, which led the good original value of k_p, without any dependence on what occurred during heating.

KEYWORDS

Mathematical study;
Chromia-forming alloys;
High temperature oxidation;
Thermogravimetry;
Kinetic constants.

INTRODUCTION

Oxidation is a phenomenon which affects all metals and metallic alloys since they all tend to give their valence electrons. This is thermodynamically inescapable. This is true when immersed in many liquid solutions but also in dry air. In the later case oxidation by O_2 is however extremely slow at room temperature but the oxidation rate rapidly increases with temperature. At elevated temperature, the oxidation rate increase rapidly, often according to an Arrhenian dependence versus temperature and total destruction of the metal of alloy occurs soon if not protected by special coating. The alloy may itself efficiently resist oxidation at high temperature if alloyed with some elements playing a particular role in this field, as aluminium, silicon or chromium. Indeed, when present in sufficiently high quantities in the alloys, these elements preferentially oxidize which leads to the development of an external oxide scale of alumina (Al_2O_3), silica (SiO_2) or chromia (Cr_2O_3). These scales are impervious to the diffusion of ionic species involved of in oxidation (metallic cations and O^{2-} anions). The latter is particularly important in the chemical composition of some superalloys[1-4] since it brings remarkable resistance not only against high temperature oxidation by gases, but also against corrosion by aggressive molten substances[5, 6]. When present in sufficient quantities (20wt.% in Ni-based alloys, 30wt.% in Co-based alloys, typically) it allows the development and the maintenance of a continuous oxide scale of chromia all around the alloy. Although less efficient than alumina as barrier for the O^{2-} anions and metallic cations, this chromia oxide significantly limits this ionic diffusion and then slows down the oxidation progress and the alloy deterioration, and delays the catastrophic oxidation.

The oxidation kinetic is often characterized by thermogravimetry since the addition of oxygen atoms to an alloy sample induces a mass gain for it. Continuously measuring the mass of a sample exposed to air (or other oxidant gas) in the hot zone of a furnace allows describing and quantifying the progress of its oxidation. This leads for example to demonstrate that the mass gain, and thus the oxidation progress, is linear in some cases (catastrophic oxidation), or that it is parabolic (mass gain proportional to the square root of time, eq. 1) when a continuous protective oxide layer exists and isolates the alloy from hot gas the thickness of which increases to slow down more and more the oxidation.

$$\frac{\Delta m}{S} = C^{st} \times \sqrt{t} \qquad (1)$$

in which Δm is the mass gain by oxidation, S the surface all around the sample, C^{st} a constant depending on the alloy, the gas nature, its pressure and the temperature, and t time.

When the mass gain is parabolic the kinetic can be described by the parabolic constant k_p (eq. 2):

$$\frac{\Delta m}{S} = \sqrt{2 \times k_p} \times t^{\frac{1}{2}} \quad \text{(Wagner's law)} \qquad (2)$$

However the determination of k_p must be carefully realized since some phenomena may induce more or less important errors on the obtained values with as consequence an underestimation of the real rate of deterioration by oxidation and consequently of lifetime of components constituted on the studied alloy.

The purpose of this work is precisely to mathematically study the consequences of such phenomena on the values of the determined parabolic constant k_p.

EXPERIMENTAL

No specific material will be used in this work which is a purely theoretic one, except a DELL Latitude E6430 portable computer.

One of the phenomena which may pose a problem for an accurate determination of a parabolic constant is the thickness already formed before temperature reaches the isothermal stage one. Indeed the heating up to the isothermal temperature is often achieved in the same atmosphere as for the oxidation test; the practical cases for which the heating is done in argon before switching to air when the targeted temperature is obtained are rather rare in practice. So, in a first time, one will explore the possible consequences of different thicknesses of oxide externally formed on the surface of a sample during heating in the same oxidant gas in which the isothermal stage will be realized. This will be done by first valuing the possible amounts of oxide resulting from the heating up to different temperatures and also the influence of the constant heating rate applied. This will be done by assuming that the instantaneous mass gain depends on temperature according to an Arrhenius law, and by calculating then plotting step by step a virtual mass gain with temperature increasing to different isothermal stage temperatures.

A second phenomenon which may threaten the accuracy of the classically determined parabolic constants is the volatilization of chromia. Indeed, when temperature is higher than 1000°C the external part of the chromia (degree III) scale may be oxidized again by oxygen contained in the hot air, according to the following reaction equation: $\frac{1}{2}\ Cr_2O_3\ (s) + {}^{3}/4\ O_2\ (g) \rightarrow CrO_3\ (g)$. This new chromium oxide (degree VI) being gaseous at these temperature it leaves the oxidizing sample. This necessarily tends to underestimate the mass gain and then the determined value of the parabolic constant.

Thereafter several virtual parabolic mass gains will be calculated and plotted, then classically analysed to extract the values of k_p, for different mass gains at heating, different real values of k_p, different values of another kinetic constant (k_v) which characterizes the rate of chromia volatilization and different times of isothermal exposure. The obtained values and their comparison with the real ones will be analysed versus the input data.

RESULTS AND DISCUSSION

Preliminary work

Before studying how the parabolic constant may evolve versus the initial mass gain achieved during heating it is important to know the order of magnitude of this one for several set of conditions. Thus, in a first time, some typical values were assessed. For that one can remind that the instantaneous linear mass gain rate may sometimes depend on temperature according to an Arrhenius law. This was encountered in the case of a Ni-30wt.%Cr alloy oxidized at 1000, 1100, 1200 and 1300°C in dry synthetic air[7] as suggested by the Arrhenian dependence on temperature of the remaining linear mass gain rates still existing for a short time in the early beginning of the isothermal stage just after the heating. Since this is precisely a real chromia–forming behaviour which was observed for this alloy at all temperatures, the Arrhenius parameters determined in this earlier work for the linear constant k_l defined by (eqs. 3 and 4) can be used here:

$$k_l(T) = \left.\frac{d(\frac{\Delta m}{S})}{dt}\right\rangle_T \qquad (3)$$

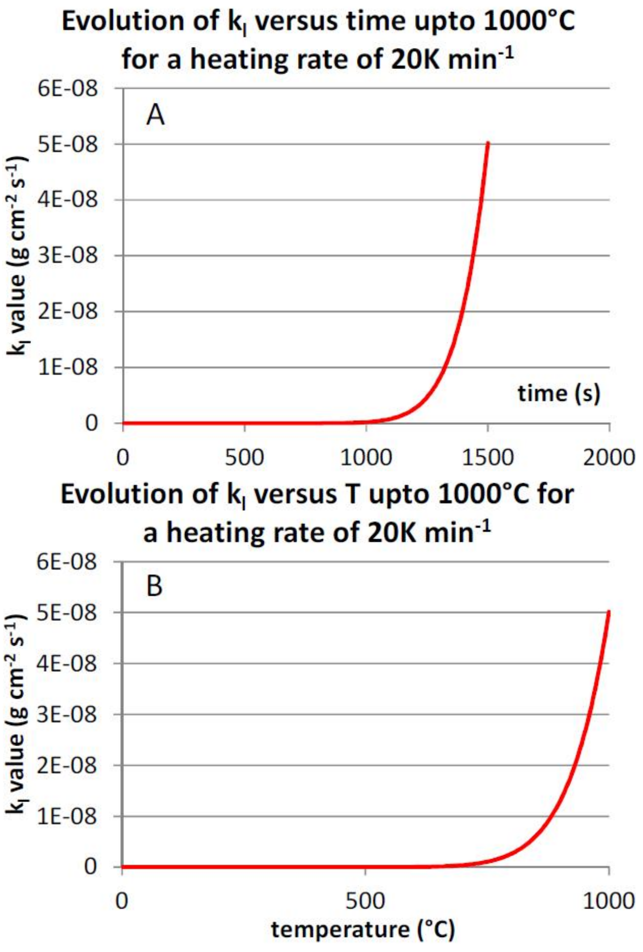
$$k_l(T) = C^{st\prime} \times e^{\left(\frac{-Q}{R\times T}\right)} \qquad (4)$$

with $C^{st'}$ = constant depending on the alloy and on the oxidant atmosphere = 0.357 g cm^{-2} s^{-1}[7], Q = activation energy = 167 kJ mol^{-1} and R = coefficient of the state law of the perfect gases = 8.314 J mol^{-1} K^{-1}.

The evolutions of the linear constant k_l versus time (A) and versus temperature (B) are shown in Figure 1. When temperature increases from the ambient temperature the linear oxidation remains extremely small for a long time, before starting increasing significantly and thereafter accelerating more and more, thanks to the exponential function in (eq. 4).

Figure 2 A (time) and B (temperature) shows that the mass gain during achieved each time step calculated using (eq. 5) logically follows the same evolutions versus time and temperature, as well as the cumulative mass gain calculated according to (eq. 6).

$$\delta\left(\frac{\Delta m}{S}\right)_T = k_l(T) \times \delta t \qquad (5)$$


Evolution of k_l versus time upto 1000°C for a heating rate of 20K min^{-1}

Evolution of k_l versus T upto 1000°C for a heating rate of 20K min^{-1}

Figure 1 : Evolution of the linear k_l constant during heating, plotted versus time (A) and versus temperature (B)

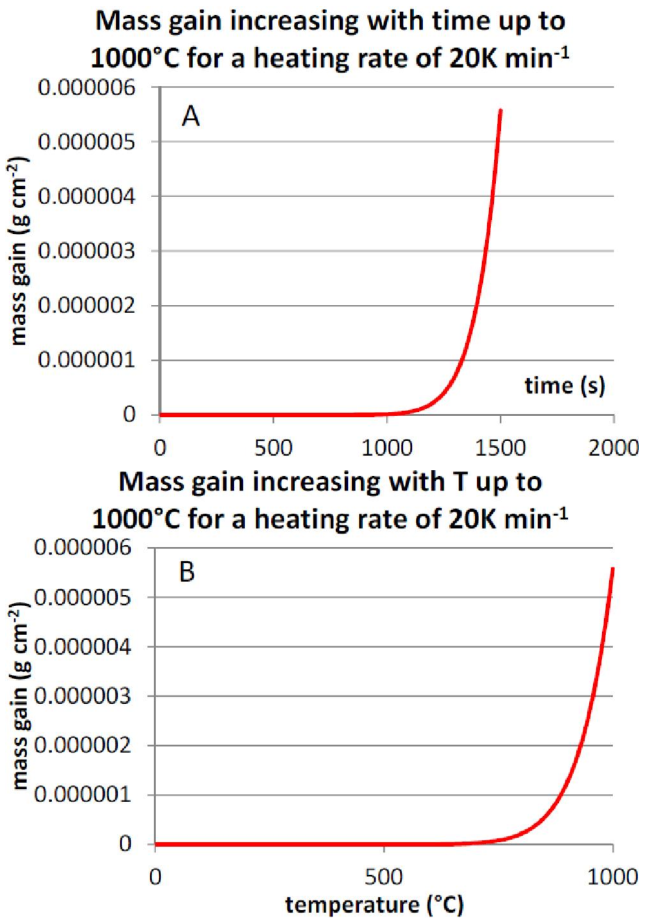


Figure 2 : Evolution of the cumulative mass gain constant during heating, plotted versus time (A) and versus temperature (B)

$$\frac{\Delta m}{S}(T+\delta \mathrm{T}) = \frac{\Delta m}{S}(T+v\times\delta t) = \frac{\Delta m}{S}(T) + k_l\,(T)\times\delta t \qquad (6)$$

where v is the heating rate, δt is the time step and δT the increase in temperature during δt.

Thus, if the value taken for the time step does not influence the mass gain kinetic during the beginning of heating its importance becomes extreme when temperature has become high enough. The dependence of the total mass gain achieved calculated for two stage temperatures (1000°C in Figure 3 and 1200°C in Figure 4) on the time step is illustrated by graphs presenting four curves together for four different heating rates.

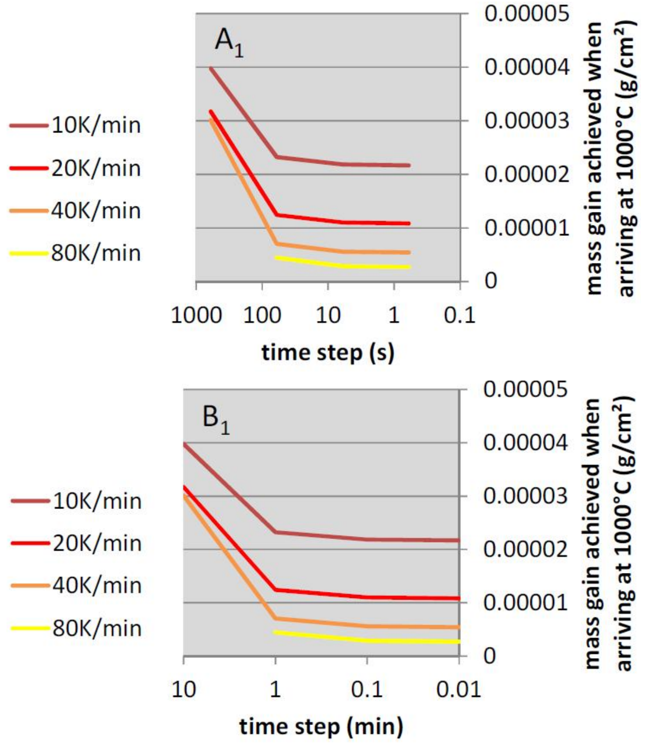


Figure 3 : Dependence of the total mass gain achieved during the whole heating when reaching 1000°C, versus time step in seconds (A_1) and in minutes (B_1)

One can first verify that, for a given heating rate and a given time step, the cumulative mass gain is well higher for a higher isothermal temperature. Second the heating rate has logically an importance since when this rate is lower the time spent at each temperature level is higher and consequently the total mass gain is more important. Third, the time step may itself significantly influence the total mass gain. But it appears that when the time step is sufficiently small there is almost no real influence: great influence in the [60, 600 s] (i.e.[1, 10 min]) range but little influence under 60s (i.e. 1min). For the calculation of the mass gain achieved during heating one choose 6s (i.e. 0.1 min). Of course all these preliminary results are potentially strongly dependent on the used Arrhenius parameters K and Q.

Influence of the mass gain achieved during heating on the obtained k_p values

The preliminary mass gain achieved during heating, as well as additionally the one which can result from pre-parabolic isothermal linear oxidation, may influence the values of k_p classically determined by plotting the mass gain (frequently re-initialized at 0 at the beginning of the isothermal stage) versus the square root of time (also taken at 0 at the beginning

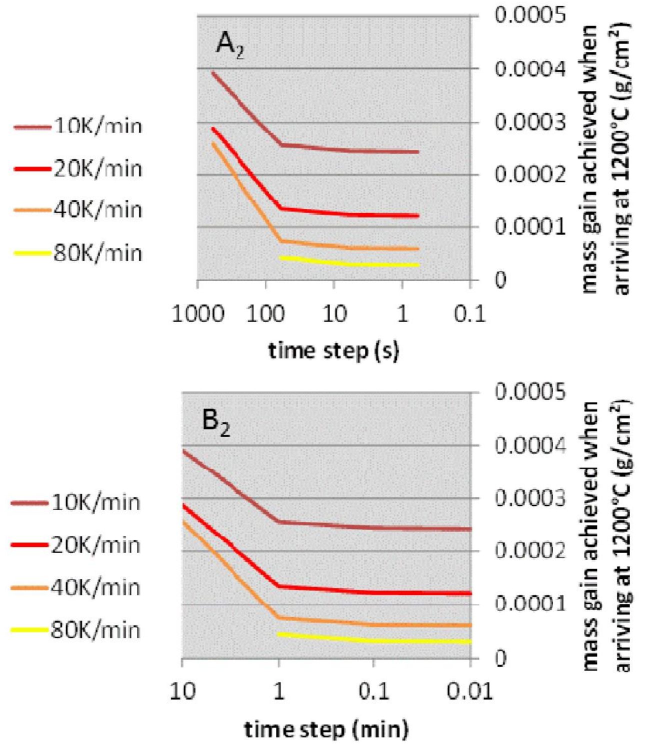


Figure 4 : Dependence of the total mass gain achieved during the whole heating when reaching 1200°C, versus time step in seconds (A_2) and in minutes (B_2)

of the isothermal stage) (eq. 7) or the square of the (re-initialized) mass gain versus time (eq. 8).

$$\frac{\Delta m}{S} = \sqrt{2 \times k_p} \times t^{\frac{1}{2}} \qquad (7)$$

$$\left(\frac{\Delta m}{S}\right)^2 = (2 \times k_p) \times t \text{ or}$$

$$\frac{1}{2}\left(\frac{\Delta m}{S}\right)^2 = k_p \times t \qquad (8)$$

In both cases the values of the parabolic constant may be thus easily deduced from the slopes of the obtained curves which are generally straight lines. But this is not really correct since, at the beginning of the isothermal stage a first thickness of external oxide (chromia here) exists (corresponding to an initial mass noted m_0) and already slows down the rate according to the Wagner's law (eqs. 2, 3 and 7). One can easily take into account this first oxide thickness by writing the differential version of the Wagner's law after correction (addition of m_0 to the Δm counted only counted from the isothermal stage start) (eq. 9) and by modifying it by eqs. 10 (more correct than eq. 9), 11 (since m0 is constant) and 12 successively:

$$d\left(\frac{\Delta m}{S}\right) = \frac{k_p}{\frac{\Delta m}{S}} \times dt \qquad (9)$$

$$d\left(\frac{\Delta m}{S}\right) = \frac{k_p}{\frac{(\Delta m + m_0)}{S}} \times dt \qquad (10)$$

$$d\left(\frac{\Delta m + m_0}{S}\right) = \frac{k_p}{\frac{(\Delta m + m_0)}{S}} \times dt \qquad (11)$$

$$\left(\frac{\Delta m + m_0}{S}\right) \times d\left(\frac{\Delta m + m_0}{S}\right) = k_p \times dt \qquad (12)$$

$$d\left[\frac{1}{2}\left(\frac{\Delta m + m_0}{S}\right)^2\right] = k_p \times dt \qquad (13)$$

The integration of eq. 13 leads to eq. 14 which can be slightly modified to give eq. 15 with which one can see that plotting the first member versus t leads to the real value of k_p: it is the slope of the curve which ought to be a straight line.

$$\frac{1}{2}\left(\frac{\Delta m + m_0}{S}\right)^2 = k_p \times t + \frac{1}{2}\left(\frac{m_0}{S}\right)^2 \qquad (14)$$

$$\frac{1}{2}\left(\frac{\Delta m + m_0}{S}\right)^2 - \frac{1}{2}\left(\frac{m_0}{S}\right)^2 = k_p \times t \qquad (15)$$

Five virtual plots of mass gain versus time were performed for simulating the isothermal parabolic oxidation of a chromia-forming alloy (Ni-30wt.%Cr for instance) in dry air at 1200°C for 100 hours, for values of oxide mass already obtained during heating (m_0) ranging from 125 µg/cm² (≈ the 123 µg/cm² for a heating rate of 20 K/min and a time step of 6s assessed above from the arrhenian data earlier obtained[7]: Q=167 kJ/mol…) to 2000 µg/cm², using a parabolic constant value of 70 ×10^{-12} g^2 cm^{-4} s^{-1} close

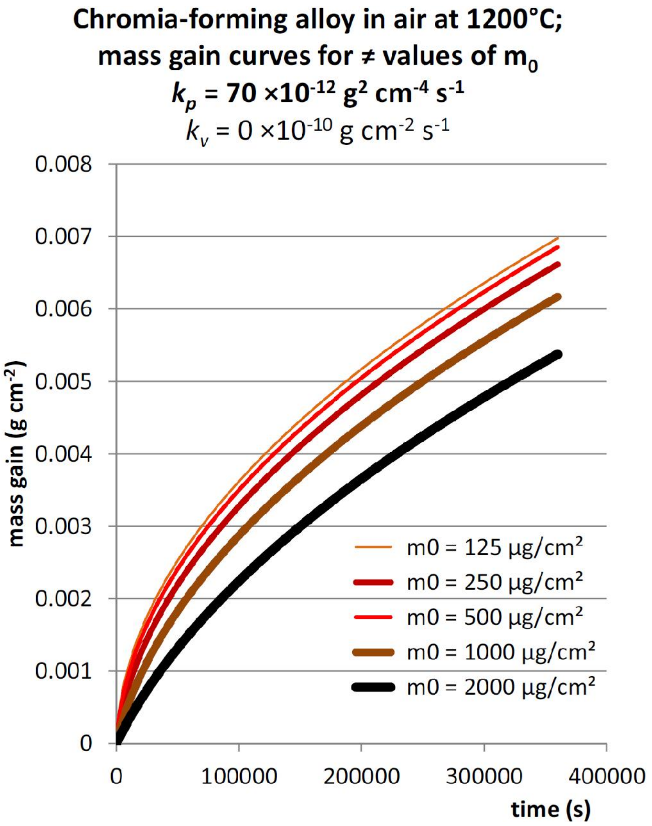


Figure 5 : Virtual mass gain curves for a chromia-forming Ni-30wt.%Cr alloy built using the k_p and k_v values inserted in the figure's top[7] using several values of mass gain obtained during heating ranging from 0.125 to 2 mg/cm² (see legend)

to the 67×10^{-12} g^2 cm^{-4} s^{-1} experimentally determined for a Ni-30wt.%Cr[7].

The obtained curves are displayed together in Figure 5. One can see that, for a given k_p value, the mass gain curves which would be experimentally acquired by re-initializing both time and mass gain to 0 at the beginning of the isothermal stage, may significantly vary with what was acquired during heating in term of oxide mass. These data files were plotted according to eq. 8 (red, thick) and to eq. 15 (blue, thin) in Figure 6 (m_0 = 125 µg/cm² and 250 µg/cm²), Figure 7 (m_0 = 500 and 1000 µg/cm²), and Figure 8 top (m_0 = 2000 µg/cm²). One can see that the two methods (the classical one, eq. 8, and the one taking m_0 into account, eq. 15) lead to distinct k_p results, the difference of which increases with m_0. Furthermore the k_p value issued from the (eq. 8) method decreases when m_0 increases (Figure 8 bottom), almost linearly: -0.014 ×10^{-12} g^2 cm^{-4} s^{-1} per µg/cm² of m_0. In contrast the results obtained from the (eq. 15) method are independent on the m_0 value, and, more important, gives the good value: 70 ×10^{-12} g^2 cm^{-4} s^{-1}.

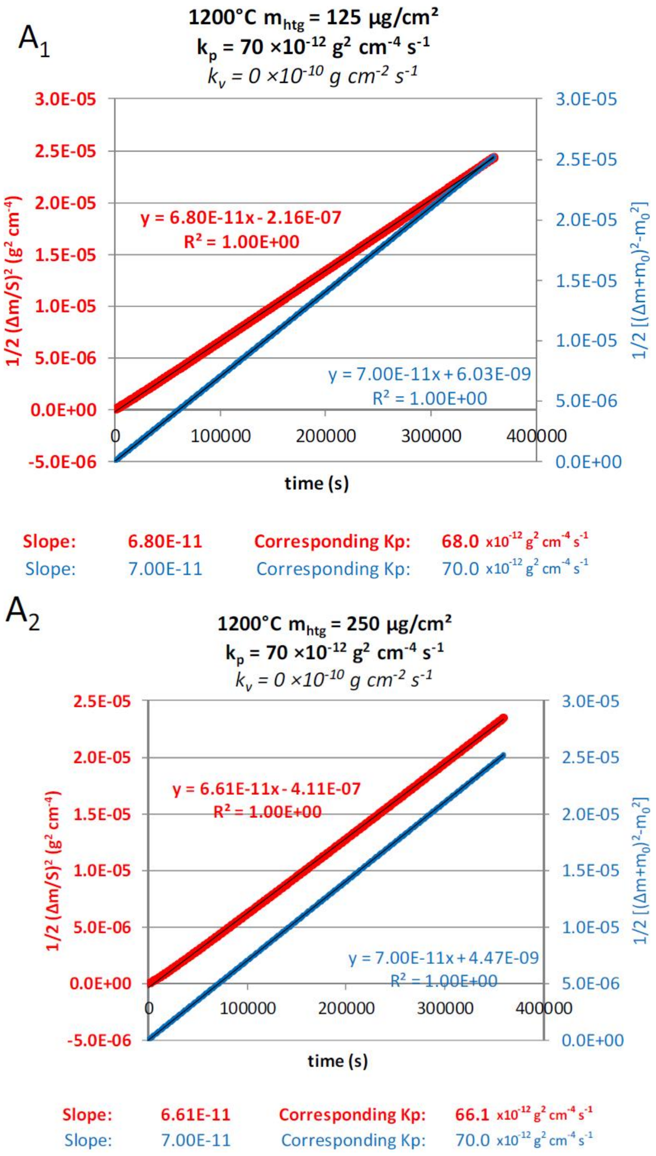
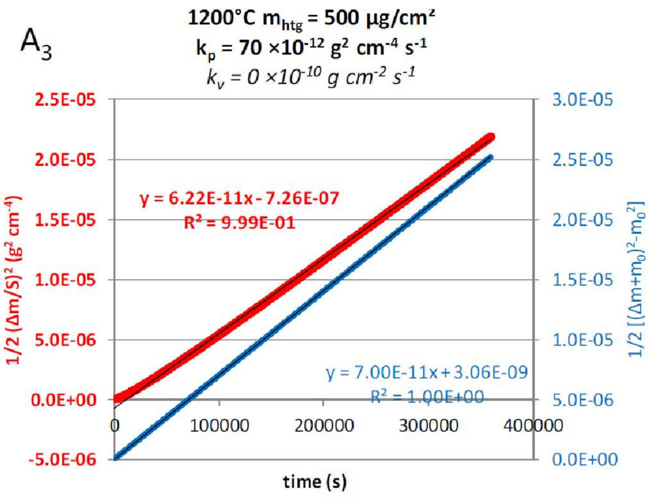


Figure 6 : (eq 8, red & thick) and (eq. 15, blue & thin) plots of the two {m_0=125 (A_1) and 250 (A_2) µg/cm²} curves of Figure 6; determination of the k_p values from the slopes of the obtained straight lines

General commentaries

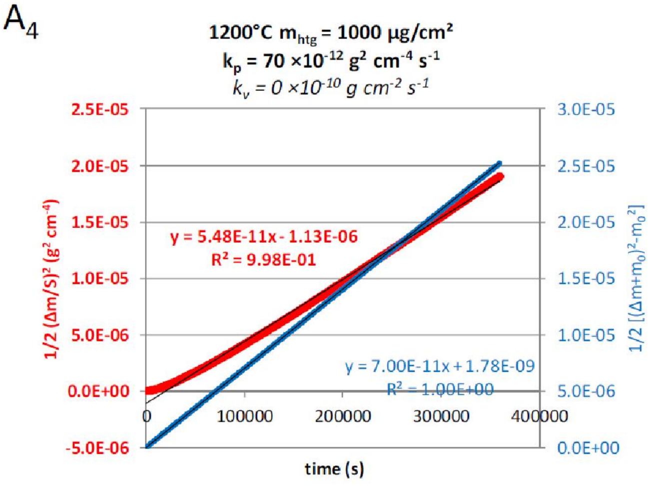
Thus, oxidation occurring during the heating before reaching the isothermal stage induces initial oxidation and mass gain which are extremely slow when temperature is still rather low. But it may become

Significantly fast at higher temperature. This was illustrated here by assuming, then exploiting, the fact



Slope: 6.22E-11 **Corresponding Kp:** 62.2 $\times10^{-12}$ g² cm^{-4} s^{-1}

Slope: 7.00E-11 Corresponding Kp: 70.0 $\times10^{-12}$ g² cm^{-4} s^{-1}

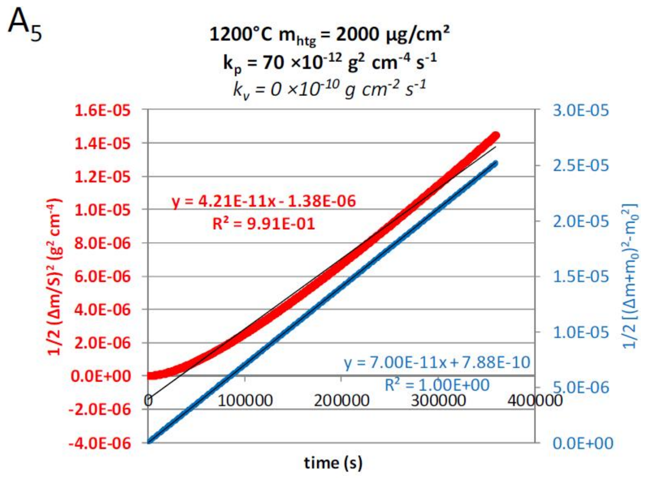


Slope: 5.48E-11 **Corresponding Kp:** 54.82 $\times10^{-12}$ g² cm^{-4} s^{-1}

Slope: 7.00E-11 Corresponding Kp: 70.01 $\times10^{-12}$ g² cm^{-4} s^{-1}

Figure 7 : (eq 8, red & thick) and (eq. 15, blue & thin) plots of the two {m_0=500 (A_3) and 1000 (A_4) µg/cm²} curves of Figure 6; determination of the k_p values from the slopes of the obtained straight lines

that the instantaneous constant often obeys an Arrhenius law. The amount of oxide formed when reaching the targeted temperature of isothermal stage depends not only on the alloy and the atmosphere, but also on the experimental parameters such as the heating rate. The accuracy of the determination of the mass gain achieved during the whole heating also depends on the frequency with which the mass gain are acquired and recorded.



Slope: 4.21E-11 **Corresponding Kp:** 42.1 $\times10^{-12}$ g² cm^{-4} s^{-1}

Slope: 7.00E-11 Corresponding Kp: 70.01 $\times10^{-12}$ g² cm^{-4} s^{-1}

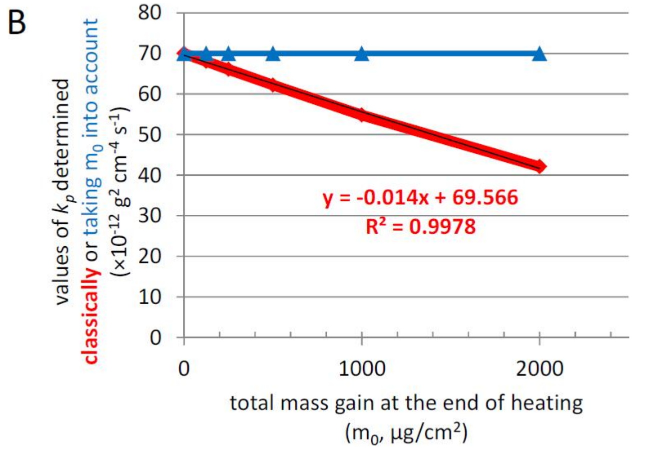


Figure 8 : (eq 8, red & thick) and (eq. 15, blue & thin) plots of the {m_0=2000 µg/cm² (A_5)} curve of Figure 6; determination of the k_p values from the slopes of the obtained straight lines; B: evolution with m_0 of the parabolic constants issued from the two equations

This initial mass gain already existing when the thermogravimetry results are usually considered (re-initialization of mass variation and time to 0) is to be seriously taken into account, especially when the mass or thickness of oxide achieved during heating are significant. Simply plotting, versus time (or the square root of time), the square of the re-initialized mass gain (respectively the mass gain) may lead to underestimated values of the parabolic constant, as demonstrated here with virtual data generated from a well-known value of *kp*. In contrast, the second method presented here faithfully gave the good initial value of *kp*. The second method is thus to be preferred to the first one, but it is true that it necessitates to know the mass of oxide obtained during the heating only (double equilibrated thermo-balance, assessment of Arrhenius parameters for the instantaneous linear constant…).

To finish one can add that, in the case of chromia specifically, the volatilization of this oxide above 1000°C (as here where 1200°C was considered) which was evocated above, needs to be also taken into account. This is the reason why the place was reserved for not zero values of the volatilization constant k_v in some graphs. The k_p value used for this work was a real k_p value, corrected from volatilization.

CONCLUSIONS

In order to do not underestimate the parabolic constant and to allow good predictions over much longer durations for real applications than for the thermogravimetry tests often shorter, and thus the lifetime of the concerned component, the *kp* constant need to be carefully determined to obtain accurate values. This work, only virtually realized, demonstrated that other methods must be preferred to the most often used one. Chromia-forming alloys were especially considered here because this was experimental data about a Ni30wt.%Cr alloy which were used as support. But this work also concerns alumina-forming alloys, silica-forming alloys, and even alloys rapidly oxidizing since not protected by the previous oxides: the only requirement is that the oxide formed is single, external and wholly covers the sample.

Future extension of this numerical work will be the case where chromia volatilization affects the mass gains and deforms the thermogravimetry curves.

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REFERENCES

[1] C.T.Sims, W.J.Hagel; 'The Superalloys', John Wiley and Sons, New York, **(1972)**.

[2] A.M.Beltram, in C.T.Sims, N.S.Stoloff, W.C.Hagel; 'Superalloy II – High temperature materials for aerospace and industrial power', John Wiley, 135 **(1987)**.

[3] E.F.Bradley; 'Superalloys: A technical guide" (1st Edition), ASM International, Metals Park, **(1988)**.

[4] M.J.Donachie, S.J.Donachie; 'Superalloys: A technical guide" (2nd Edition), ASM international, materials park, **(2002)**.

[5] P.Kofstad; 'High temperature corrosion', Elsevier applied science, London, **(1988)**.

[6] J.Young; 'High temperature oxidation and corrosion of metals', Elsevier, Amsterdam, **(2008)**.

[7] P.Berthod; Oxidation of Metals, **64(3/4)**, 235 **(2005)**.