

Mathematical study of the effects of the mass gain achieved during heating and of the mass loss by Cr_2O_3 volatilization on the constants characterizing the high temperature oxidation rate of chromia-forming alloys

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ABSTRACT

After a first recently presented numerical work concerning the effect of the existence of an initial mass gain – for example achieved during the heating up to the stage temperature – on the determined values of the parabolic constant, the present study is devoted to the influence of the same initial mass gain on the couple of kinetic values describing the thickening of the chromia external scale (k_p) on Cr-rich alloys as well as the volatilization of a part of this oxide when temperature is high enough to allow having a significant chromia loss by this phenomenon (k_v). For that several theoretical mass gains were built from values of kinetic constants selected in the available experimentally determined ones, for different values of mass gain at heating chosen in a range of credible values. It appeared that an initial mass gain effectively influences the values of k_p and k_v determined according to the $\{(\Delta m/S) \times d(\Delta m/S)/dt = k_p - k_v \times m\}$ method. The higher the initial mass gain the farer the obtained values by comparison with the injected ones. In contrast, if the initial mass gain is taken into account the exact values of the injected k_p and k_v are found. © 2016 Trade Science Inc. - INDIA

KEYWORDS

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

INTRODUCTION

The kinetic analysis of the high temperature oxidation progress can be done by thermogravimetry, which is a more continuous method than the cross-sectional metallography characterization on oxidized samples after exposures interrupted at different times. Usually the plot of mass gain per surface unit area

$(\Delta m/S)$ versus time (t) according to one of the two following equations (eqs.1&2) allows the determination of the value of the parabolic constant noted k_p intervening in the Wagner’s law (its most simplified version: eq. 3).

$$\frac{\Delta m}{S} = f(\sqrt{t}) \quad (1)$$

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$$\left(\frac{\Delta m}{S}\right)^2 = f(t) \quad (2)$$

$$\frac{\Delta m}{S} = \sqrt{2 \times k_p \times t^{\frac{1}{2}}} \quad (3)$$

When this determination can be carried out without any problem the values of parabolic constant allow predicting the mass gain by oxidation for times much longer than the test duration, as is to say anticipating the oxidation resistance of the alloy in long service. The lower the k_p value the better the oxidation resistance, as demonstrated by the usual values of k_p obtained for alumina-forming, chromia-forming and silica forming alloys which are several orders of magnitude lower than for pure cobalt, nickel or iron for similar oxidizing atmospheres and temperatures. Refractory metallic alloys and superalloys are for these reasons, rich in aluminium, chromium or silicon to promote the formation of an external continuous protective oxide scale^[1-4]. Chromia-rich alloys are additionally also resistant against hot corrosion^[5-6].

Unfortunately the classical determination of the parabolic constant can be influenced by the amount of oxide formed before considering the initial time and mass gain, both taken as being zero at the beginning of the isothermal stage. Furthermore, specifically in the case of the chromia-forming alloys, another phenomenon is to be taken into account to extract the real value of k_p from the mass gain measurements: the volatilization of chromia. Indeed, chromia tends to be re-oxidized into another oxide when temperature is high enough (higher than 1000°C in air at $P=1$ atm.) and this new one is gaseous at the considered temperatures. Thus, its formation systematically minimizes the mass gain and thus the value of k_p when classically determined.

In this second experiments-free work (after a first one in press^[7]), a mathematical study using typical values of experimental mass gain kinetics was undertaken to analyse the dependence of the kinetic constants of oxidation on the preliminary mass gain at heating and on the volatilization phenomenon.

EXPERIMENTAL

Here too, no specific material was involved in this purely theoretic work. Only a DELL Latitude E6430 portable computer supporting the 2010-version Excel software of Microsoft was used. A series of theoretical mass gain curves of different types were plotted then analysed using likely kinetic constants values. The involved equations will be presented all along the results.

RESULTS AND DISCUSSION

Preliminary simulation of the effect of chromia volatilization

The reaction according to which chromia may be oxidized once again to become a gaseous oxide is described by the following chemical equation: $\frac{1}{2} \text{Cr}_2\text{O}_3$ (solid) + $\frac{3}{4} \text{O}_2$ (gas) \rightarrow CrO_3 (gas). The resulting loss in mass per surface unit area obeys a linear law (eq. 4) involving a new constant usually noted k_v .

$$\begin{aligned} 1200^\circ\text{C } m_{\text{htg}} &= 123 \mu\text{g}/\text{cm}^2 \\ K_p &= 70 \times 10^{-12} \text{ g}^2 \text{ cm}^{-4} \text{ s}^{-1} \\ K_v &= 0 \text{ to } 1000 \times 10^{-10} \text{ g cm}^{-2} \text{ s}^{-1} \end{aligned}$$

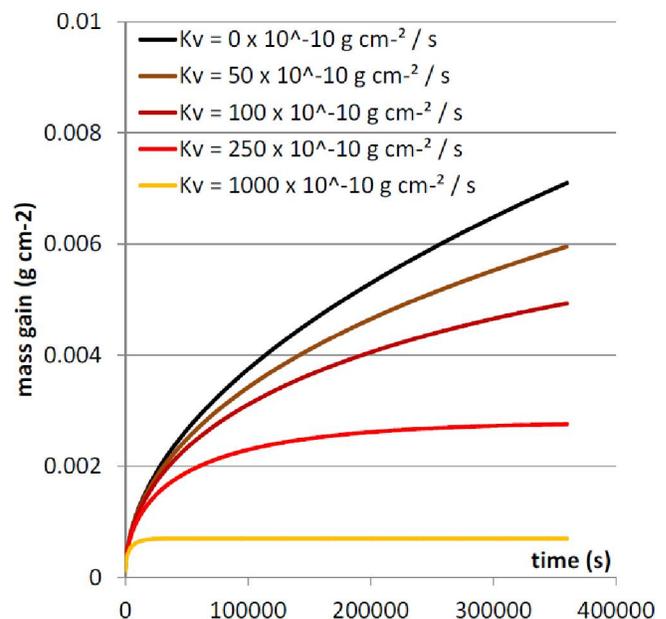


Figure 1 : Evolution of the theoretic mass gain curves with the value of the linear constant characterizing the mass loss due to the volatilization of chromia

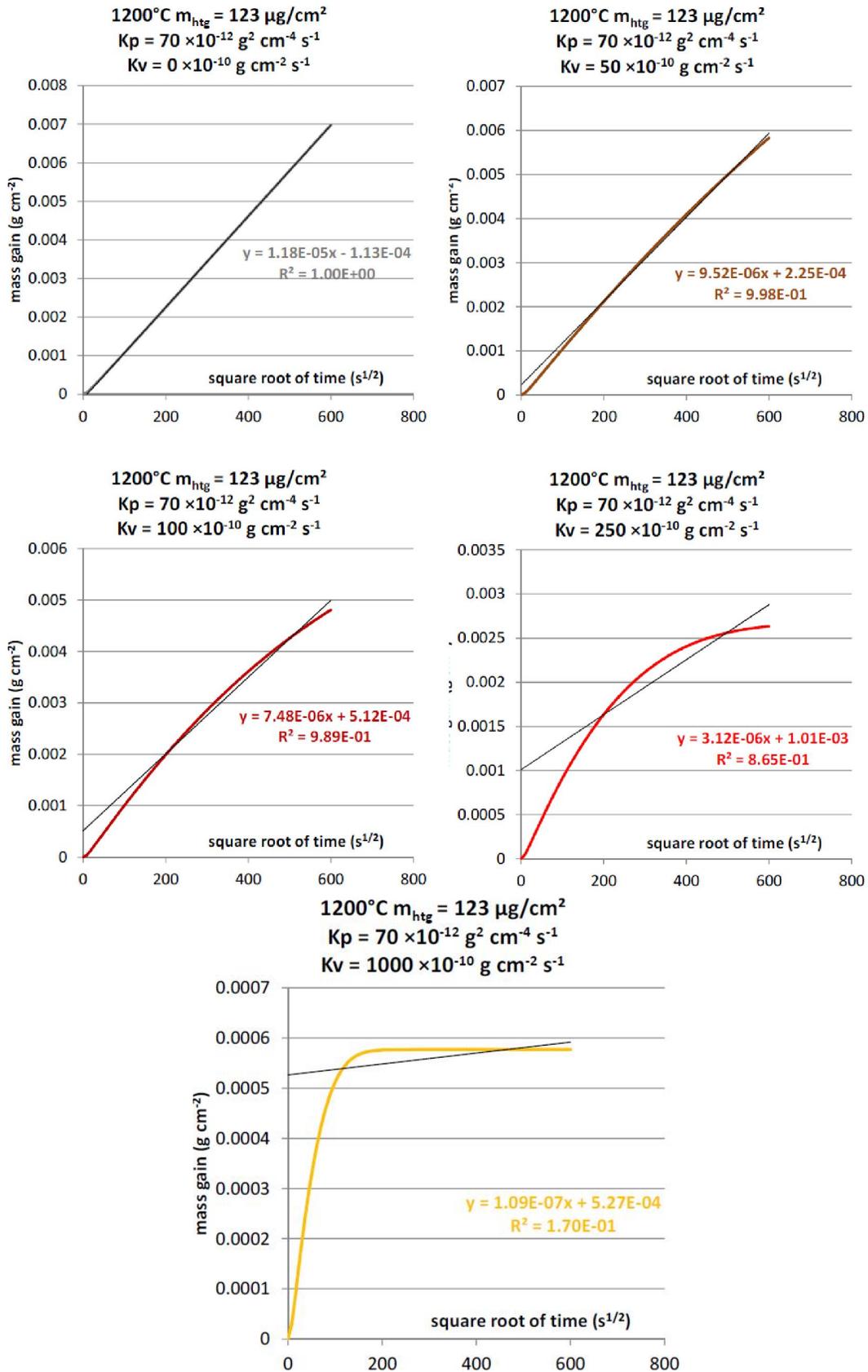


Figure 2 : Influence of the value of the k_v constant on the shape of the {mass gain versus square root of time} curves and on the regression straight line slope (thus on the deduced k_p value)

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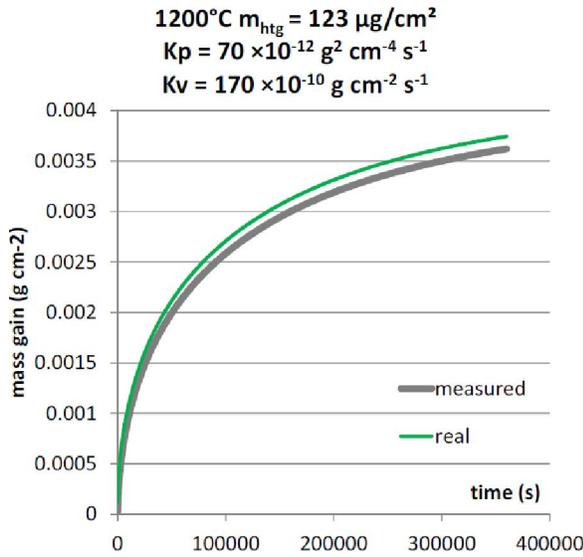
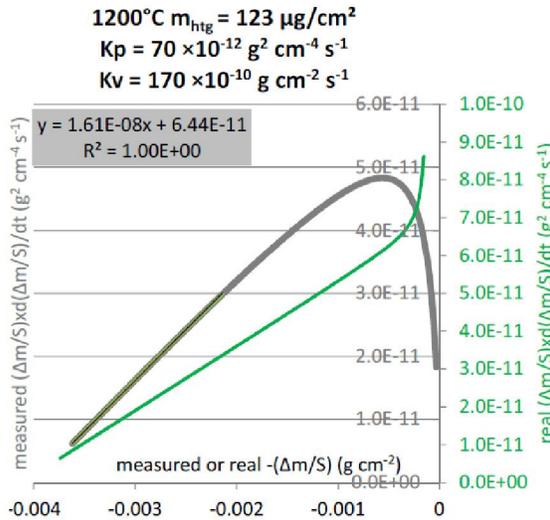


Figure 3 : Effect on the isothermal mass gain curve of the preliminary mass gain obtained until the end of heating (thick grey curve: mass gain at heating not taken into account, thin green curve: 0.123mg/cm² used in the equation)



2 s^{-1} obtained in the following conditions: Ni-30wt.%Cr binary cast alloy, synthetic 80%N₂-20%O₂ dry air, 1200°C.

The simulated curves were built by calculating the successive values of additional mass gain, according to the following equations (eqs. 5&6) in which $\Delta m/S|_n$ is the mass gain at the instant $t_n = n \times \delta t$, and δt the incremental time step:

$$\frac{\Delta m}{S} \Big|_{n+1} = \frac{\Delta m}{S} \Big|_n + \delta \left(\frac{\Delta m}{S} \right) \Big|_n \quad (5)$$

With

$$\delta \left(\frac{\Delta m}{S} \right) \Big|_n = \left(\frac{k_p}{\frac{\Delta m}{S} \Big|_n} - k_v \right) \times \delta t \quad (6)$$

Five curves are plotted together in Figure 1, from

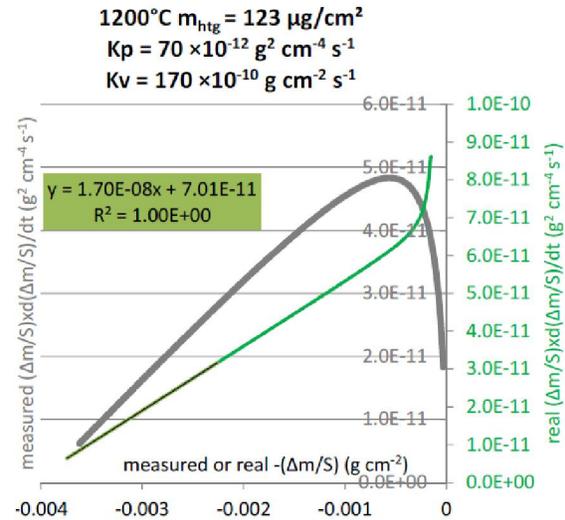


Figure 4 : Both graphs: $\left\{ \frac{\Delta m}{S} \times \frac{d(\frac{\Delta m}{S})}{dt} = f\left(-\frac{\Delta m}{S}\right) \right\}$ plots for the thick green curve and of the thin grey curve; left: equation of the regression straight line obtained for the thick grey curve (differences between the injected values of k_p and k_v and the deduced ones); right: regression straight line equation for the green thin curve (perfect match between the injected k_p and k_v and the determined ones)

$$\frac{\Delta m}{S} (\text{loss}) = -k_v \times t \quad (4)$$

Many values of this constant were determined in earlier works. In the present study only the values of k_v (and also of k_p and of mass gain at 20K/min heating from room temperature, noted $\Delta m_0/S$) determined in^[8] will be used as basis: $\Delta m_0/S = 123 \mu\text{g cm}^{-2}$, $k_p = 70 \times 10^{-12} \text{ g}^2 \text{ cm}^{-4} \text{ s}^{-1}$ and $k_v = 170 \times 10^{-10} \text{ g cm}^{-2} \text{ s}^{-1}$

values of k_v varying from 0 (no or negligible chromia volatilization) to $1000 \times 10^{-10} \text{ g cm}^{-2} \text{ s}^{-1}$ (very intense volatilization).

One see that when $k_v = 0 \times 10^{-10} \text{ g cm}^{-2} \text{ s}^{-1}$ the mass gain curve is really parabolic while the mass gain less and less progresses with time when k_v increases to 50 or $100 \times 10^{-10} \text{ g cm}^{-2} \text{ s}^{-1}$. The last part of the curve plotted for $k_v = 250 \times 10^{-10} \text{ g cm}^{-2} \text{ s}^{-1}$ is almost horizontal while the mass gain is horizontal

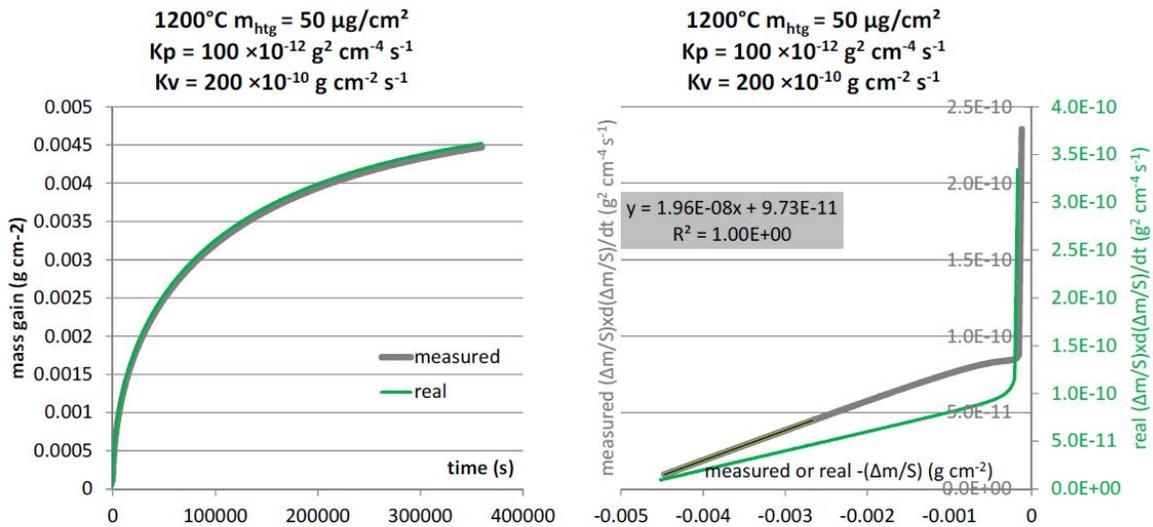


Figure 5 : Mass gain curves built without (thick grey) and with (thin green) consideration to an initial mass gain (left) and the corresponding (eq.6)-type curves (right); here initial mass gain = $50\mu\text{g}/\text{cm}^2$

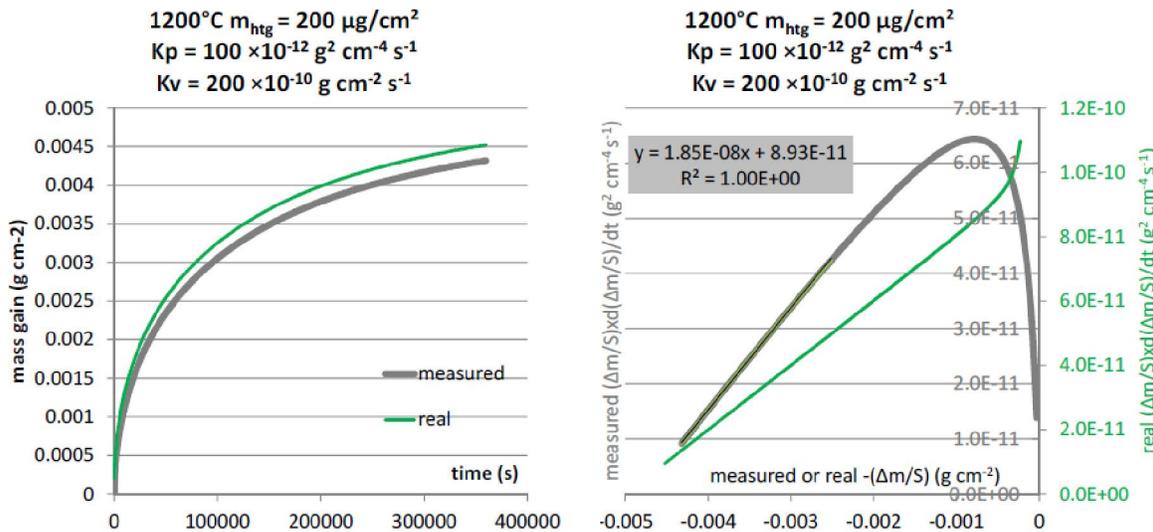


Figure 6 : Mass gain curves built without (thick grey) and with (thin green) consideration to an initial mass gain (left) and the corresponding (eq.6)-type curves (right); here initial mass gain = $200\mu\text{g}/\text{cm}^2$

on its main part for $k_v = 1000 \times 10^{-10} \text{ g cm}^{-2} \text{ s}^{-1}$: the chromia scale volatilizes as fast as it grows.

When plotted as mass gain versus the square root of time, the shape of the mass gain curve, strictly straight for no volatilization bends more and more when the injected value of k_v increases (Figure 2). Almost still straight for $k_v = 50 \times 10^{-10} \text{ g cm}^{-2} \text{ s}^{-1}$ and eventually for $k_v = 100 \times 10^{-10} \text{ g cm}^{-2} \text{ s}^{-1}$ the curve is much too bent to be considered as almost straight for $k_v = 250 \times 10^{-10} \text{ g cm}^{-2} \text{ s}^{-1}$ and more. The real case described in^[8] for a Ni-30wt.%Cr oxidized at 1200°C in air is intermediate between the two latter cases and it was compulsory to analyze the mass gain files according the method developed in this

same work^[8].

One can briefly remind here that it was demonstrated in^[8] that the two constants k_p and k_v may be simply determined by plotting the isothermal mass gain data in the (eq. 7) scheme:

$$\frac{\Delta m}{S} \times \frac{d\left(\frac{\Delta m}{S}\right)}{dt} = f\left(-\frac{\Delta m}{S}\right) \quad (7)$$

Indeed, except the first instants, this leads to a straight line whose ordinate at the origin is k_p and whose slope is k_v ^[8], as shown in (eq. 8):

$$\frac{\Delta m}{S} \times \frac{d\left(\frac{\Delta m}{S}\right)}{dt} = k_p - k_v \times \left(-\frac{\Delta m}{S}\right) \quad (8)$$

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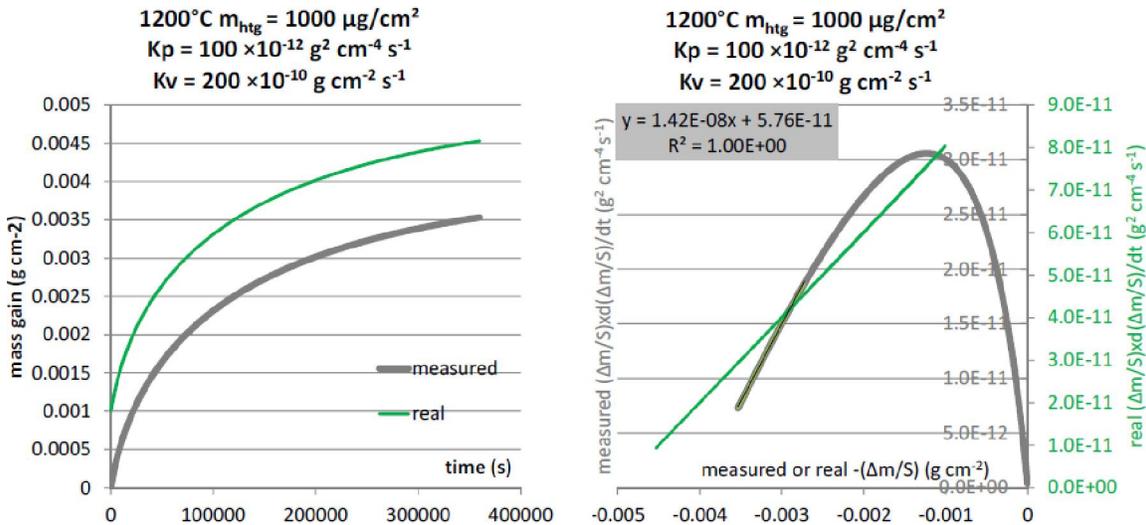


Figure 7 : Mass gain curves built without (thick grey) and with (thin green) consideration to an initial mass gain (left) and the corresponding (eq.6)-type curves (right); here initial mass gain = 1mg/cm²

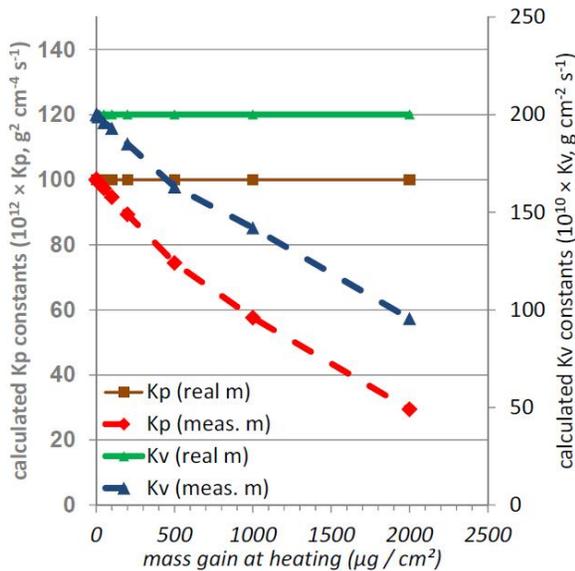


Figure 8 : Graphical representation of the lowering of the k_p & k_v (eq. 7)-determined values of the thick grey mass gain curve for which no initial mass gain curve is taken into account (dotted lines, “(meas. m)”), by regards to the initially injected values (continuous lines, “(real m)”))

Influence of the mass gain at heating on the real parabolic constant and the chromia volatilization constant

As illustrated in Figure 3, and as recently studied^[7], the mass gain achieved by oxidation during the heating may influence the mass gain curve shape (both curves plotted according to (eq.7), but thick grey curve: mass gain re-initialized to 0 at the beginning of the isothermal dwell, and thin green curve:

initial mass gain taken equal to 123µg/cm² (the green curve is simply the grey one translated over +123µg/cm² for all time). One already saw^[7] that the classically determined values of k_p may be modified because of the no consideration of this initial mass gain (under-estimation) but forgetting this mass gain at heating also may lead to not correct estimation of the parabolic constant and of the volatilization constant both issued from the (eq. 8) method. The (eq. 8)-based method gives exactly the real values of k_p and k_v in the case of the thin green curve while the ones deduced from the regression straight line equation obtained for the thick grey curve are a little different: basis: $k_p = 64.4 \times 10^{-12} \text{ g}^2 \text{ cm}^{-4} \text{ s}^{-1}$ and $k_v = 161 \times 10^{-10} \text{ g cm}^{-2} \text{ s}^{-1}$ against $k_p = 70 \times 10^{-12} \text{ g}^2 \text{ cm}^{-4} \text{ s}^{-1}$ and $k_v = 170 \times 10^{-10} \text{ g cm}^{-2} \text{ s}^{-1}$.

Similar plots are done in Figure 5 to 7. One can see that, for an increasing value of initial mass gain (multiplied by more or less 4 each time) the (eq. 6)-determined values of k_p and k_v become more and more far from the real values, while these determined values remain constantly exactly equal to the initially injected ones when the preliminary mass gain is taken into account (equations of regression straight line not presented since constantly “ $y=170E-10x + 70E-12$ ”). The study was extended to a broader range of values for the initial mass gain (0 to 2mg/cm²) and the results are graphically presented in Figure 8.

CONCLUSIONS

This work, realized without any experiments but using credible values of mass gain by high temperature oxidation since inspired from really obtained data, clearly showed that the initial mass gain must be taken into account to allow obtaining reliable values, not only of the parabolic constant as classically determined, but also of the real parabolic constant and of the chromia volatilization constant when the (eq. 5&6)-based method is applied. Knowing such initial mass gain may be not really easy to specify but experimentally heating and quenching when arriving at the stage temperature may give estimated values of the realized mass gain provided that no oxide loss occurs (or use of an alumina crucible in which the sample is). Another way is specifying the arrhenian parameters of the linear oxidation and integrating from room temperature up to the stage one. This may be difficult to do but this work demonstrated that this may be very useful to ensure a good accuracy of the determined values of k_p and k_v .

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