



How oxide detachments occurred during high temperature oxidation of a metallic alloy may influence the determination of the parabolic constant k_p ?

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ABSTRACT

The parabolic constant K_p is the most important kinetic constant characterizing the high temperature oxidation rate of superalloys. It is usually determined by plotting mass gain versus the square root of time which led, in the simplest cases where the mass gain kinetic faithfully followed the Wagner's law, to a slope to which K_p is related by a simple relationship. Unfortunately detachments of the external oxide scale occurred in most cases, with as results the existence of jumps in the mass gain curves. These ones become thus tricky to analyse for deducing K_p with accuracy. The topic of this work is to evaluate the impact of two parameters, the surface fraction affected by an oxide scale detachment and the instant at which it occurs, on the value of K_p determined classically, this by simulating mass gain curves and jumps induced by scale detachment and analysing them. © 2016 Trade Science Inc. - INDIA

KEYWORDS

High temperature oxidation;
Oxide scale detachment;
Mass gain jumps;
Kinetic constants;
Mathematical study;
Chromia-forming alloys.

INTRODUCTION

Oxidation resistant refractory alloys and superalloys are designed for allowing their auto-protection against high temperature oxidation by the development of a continuous external oxide scale, the nature of which is monitored by the chemical composition of the alloys^[1-4]. Adding significant quantities of aluminium, chromium or silicon to these alloys favours the development of alumina (Al_2O_3), chromia (Cr_2O_3) or silica (SiO_2), oxide which are more (alumina) or less (chromia) impermeable to

the diffusion of the species involved in the oxidation process (metallic cations or oxygen anions). The development of such oxides begin by nucleation and continues by lateral growth and thickening with as consequence a continuous layer isolating the alloy from the oxidant gases, but also the appearance and the increase of growth stresses which may lead, even isothermally, to unsticking of the external scale^[5,6]. Parts of the scales may fall (with a result a downfall in sample mass clearly visible in the thermogravimetry curve) or not. In this later case the part of oxide is generally cracked and gases can

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penetrate and reach the denuded alloy causing new oxidation initially very fast, concerning only a little part of the sample surface but which induces a visible jump of the mass gain curve. Chromia, otherwise affected by other phenomena such as volatilization^[7], is also particularly concerned by such phenomenon which is frequently encountered for chromium-rich alloys and chiefly with chromium-based alloys^[8]. After such phenomenon, the mass gain files cannot be analysed as classically done, for specifying the kinetic constants since the global measurement combine two different specific behaviours: the one of the main part of surface which carries on the initial Wagner's law from the same oxide thickness, and the one of the recently denuded part for which the oxidation rate is much faster even if it may also follows the same Wagner's law. After the jump, the following curve seems parabolic but it is not the case, and the classical K_p determination may lead to a not correct value of the parabolic constant.

This is this problem which is addressed in this work: how doing the best possible determination of the parabolic constant? This was done by working of artificial mass gain curves, composite curve mathematically combining two contributions: the unchanged Wagner's law one concerning a main part of the sample surface, and the specific mass gain rate on the small part of surface subject to much faster oxidation.

EXPERIMENTAL

No specific material will be used in this work which is a purely theoretic one, except a DELL Latitude E6430 portable computer. The Excel 2010 software of Microsoft was used to plot and exploit the virtual mass gain curves.

Reference curve without any jump due to oxide detachment

A first curve, not affected by any jumps due to oxide detachment, thus concerning a sample the whole surface of which permanently obeys the Wagner's law (eq. 1), was plotted according to (eq. 1) and (eq. 2),

$$\frac{\Delta m}{S}(t + dt) = \frac{\Delta m}{S}(t) + d\left(\frac{\Delta m}{S}\right) \quad (1)$$

with:

$$d\left(\frac{\Delta m}{S}\right) = \frac{K_p}{\frac{\Delta m}{S} + \frac{\Delta m_0}{S}} \times dt \quad (2)$$

and " m/S being the mass gain per surface unit area, K_p being the parabolic constant, " m_0/S the mass gain already achieved during heating and existing at the beginning of the isothermal stage, and t time.

The following numerical conditions were used:

$$\Delta m_0 / S = 125 \times 10^{-6} \text{ g cm}^{-2}$$

$$K_p = 70 \times 10^{-12} \text{ g}^2 \text{ cm}^{-4} \text{ s}^{-1}$$

$$dt = 60 \text{ seconds}$$

$$\text{Total duration} = 100 \text{ hours} = 360,000 \text{ seconds.}$$

Such parabolic curve globally obeys the following Wagner's law obtained by integration (eq. 3):

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

but more precisely the following one (eq. 4):

$$\frac{1}{2} \left(\frac{\Delta m}{S} + \frac{\Delta m_0}{S} \right)^2 - \frac{1}{2} \left(\frac{\Delta m_0}{S} \right)^2 = K_p \times t \quad (4)$$

which takes into account the initial mass gain prior to the isothermal thickening of the scale.

This one shows that K_p can be determined as the slope of the straight line resulting of the plot of the first term of equation (eq. 4) versus time.

Curves presenting a jump due to oxide detachment

After this reference curve other curves, for which an oxide scale detachment concerning a fraction ξ of the surface S occurred after a time τ counted from the beginning of the isothermal stage, were artificially built. They were plotted according to the equations (eqs. 1 and 2) from $t=0$ and $t=\tau$.

For $t > \tau$ they were plotted according to the following equations (eq. 5 to 8), by changing notation by a more practical one: $\mu = "m/S$.

$$\mu(t + dt) = \mu(t) + \frac{1}{S} \{ (1 - \xi) \times S \times d(\mu_1) + \xi \times S \times d(\mu_2) \} \quad (5)$$

as is to say :

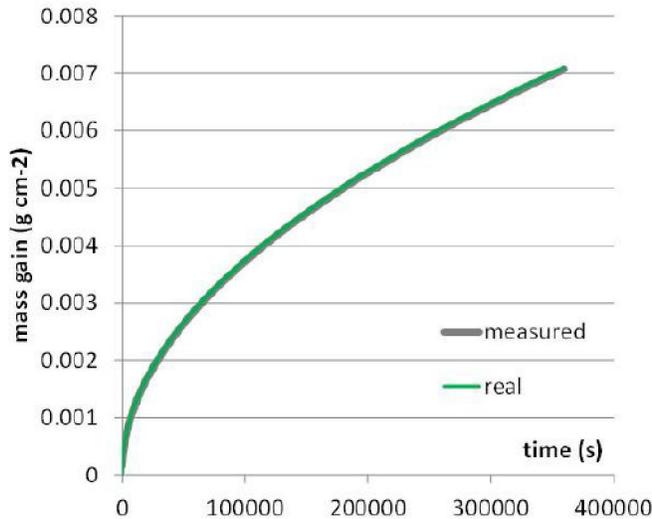
$$\mu(t + dt) = \mu(t) + (1 - \xi) \times d(\mu_1) + \xi \times d(\mu_2) \quad (6)$$

with :

$$d(\mu_1) = \frac{K_p}{d(\mu_1) + \mu_1(\tau)} \times dt \quad (7)$$

$$\xi = 0.1 \text{ (i.e. 10\% of S)}$$

$$\tau = 180,000\text{s}$$



$$d(\mu_2) = \frac{K_p}{d(\mu_2) + \mu_2(\tau)} \times dt \quad (8)$$

μ_1 is the mass gain per unit area on the part of surface $(1-\xi) \times S$ not affected by any scale detachment and μ_2 is the mass gain per unit area on the part of surface $\xi \times S$ which was affected by such scale

$$\Delta m_0 / S = 25 \text{ } \mu\text{g/cm}^2$$

$$K_p = 70 \times 10^{-12} \text{ g}^2 \text{ cm}^{-4} \text{ s}^{-1}$$

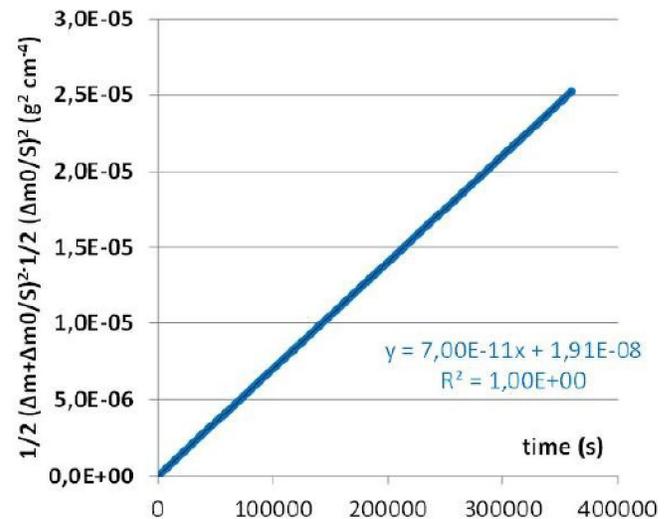
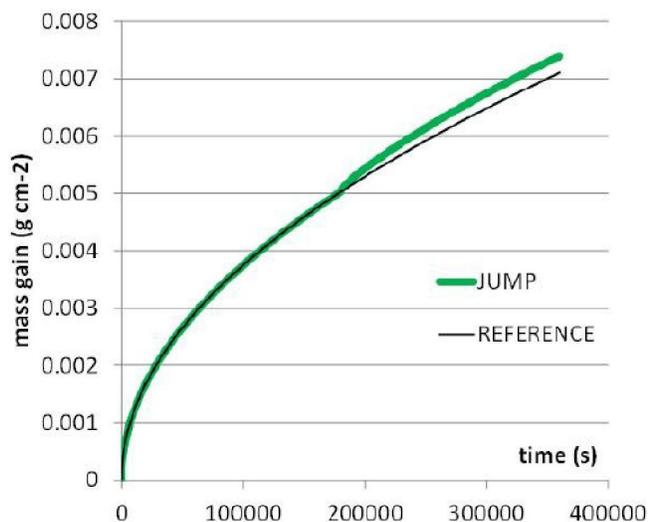


Figure 1 : The mathematical parabolic curves (left; by taking the mass gain at heating into account “real” or not “measured”) and the plot devoted to the K_p determination (right; $K_p = \text{slope} = 70 \times 10^{-12} \text{ g}^2 \text{ cm}^{-4} \text{ s}^{-1}$ as initially entered in the model)

$$\xi = 0.1 \text{ (i.e. 10\% of S)}$$

$$\tau = 180,000\text{s}$$



$$\xi = 0.1 \text{ (i.e. 10\% of S)}$$

$$\tau = 180,000\text{s}$$

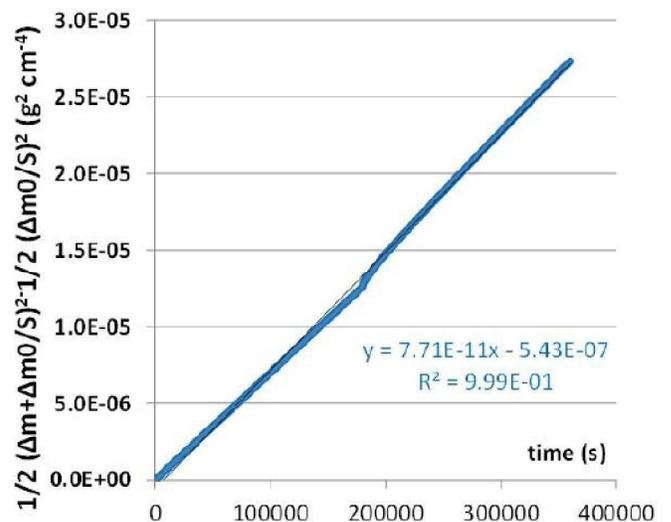


Figure 2 : The mathematical parabolic curve affected by an oxide scale detachment on 10% of the sample surface after 50 hours of isothermal oxidation (left; green thick curve plotted with the parabolic reference curve: black thin); K_p classically determined: $K_p = \text{slope} = 77.1 \times 10^{-12} \text{ g}^2 \text{ cm}^{-4} \text{ s}^{-1}$)

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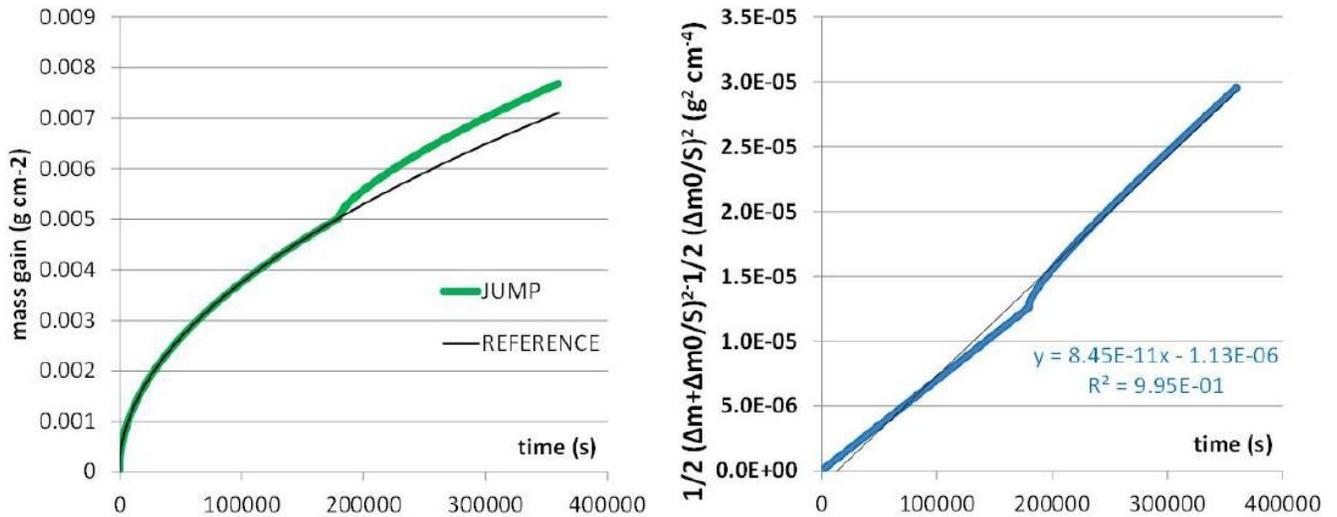


Figure 3 : The mathematical parabolic curve affected by an oxide scale detachment on 20% of the sample surface after 50 hours of isothermal oxidation (left; green thick curve plotted with the parabolic reference curve: black thin); K_p classically determined: $K_p = \text{slope} = 84.5 \times 10^{-12} \text{ g}^2 \text{ cm}^{-4} \text{ s}^{-1}$

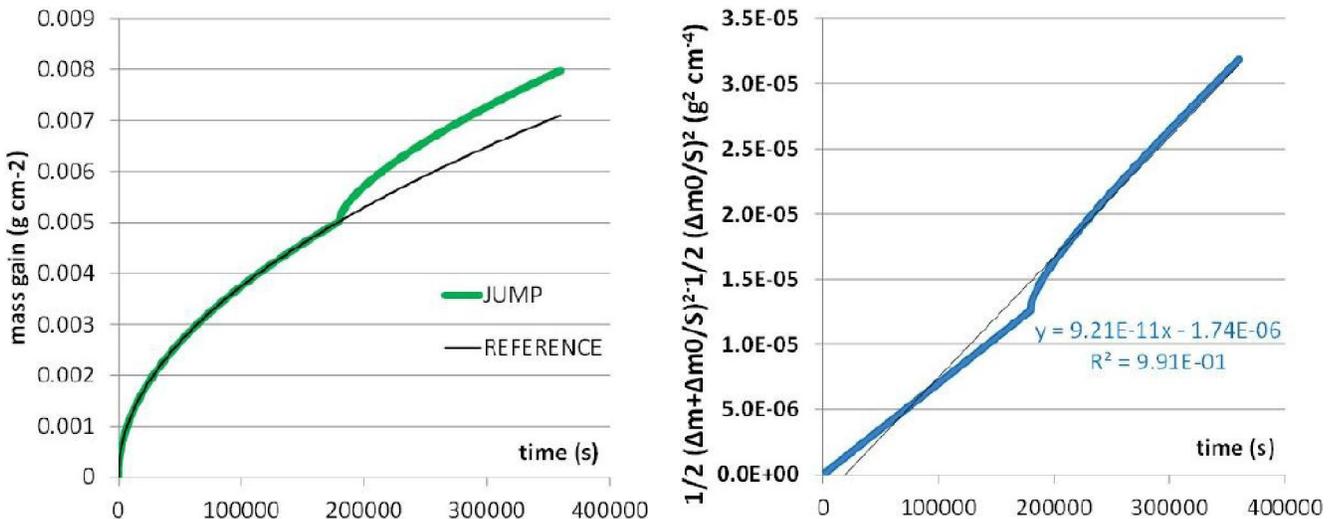


Figure 4 : The mathematical parabolic curve affected by an oxide scale detachment on 30% of the sample surface after 50 hours of isothermal oxidation (left; green thick curve plotted with the parabolic reference curve: black thin); K_p classically determined: $K_p = \text{slope} = 92.1 \times 10^{-12} \text{ g}^2 \text{ cm}^{-4} \text{ s}^{-1}$

detachment.

Since the mass gain per surface unit area was simply $\Delta m/S(\tau)$ this value is to be considered for $\mu_1(\tau)$. This is different for the value of μ_2 at the instant τ : the scale is here detached and gases are directly in contact with alloy. However, taking $\mu_2(\tau)=0$ lead an infinite value for the first step of calculation according to (eq. 8). It was thus chosen for $\mu_2(\tau)$, even if it is not really correct, to choose the same value as for the beginning of isothermal stage for all the surface: $\Delta m_0/S = 125 \times 10^{-6} \text{ g cm}^{-2}$. Thus, the “initial” conditions for the second part of oxidation ($\tau \leq t \leq 360000$ seconds), were: $\mu_1(\tau) =$

$\Delta m/S(\tau)$ and $\mu_2(\tau) = \Delta m_0/S = 125 \times 10^{-6} \text{ g cm}^{-2}$.

Several curves presenting a jump due to oxide detachment were plotted, for the following values of ξ and of τ :

$\xi = 0.1, 0.2, 0.3, 0.4$ and 0.5 (i.e. 10%, 20%, 30%, 40% and 50% of the surface)

$\tau = 25\text{h}, 50\text{h}$ and 75h

They were all analyzed according to (eq. 4') (i.e. equation (eq. 4) rewritten):

$$\frac{1}{2} \left(\mu + \frac{\Delta m_0}{S} \right)^2 - \frac{1}{2} \left(\frac{\Delta m_0}{S} \right)^2 = K_p \times t \tag{9}$$

in a first time by noting the slope of the whole

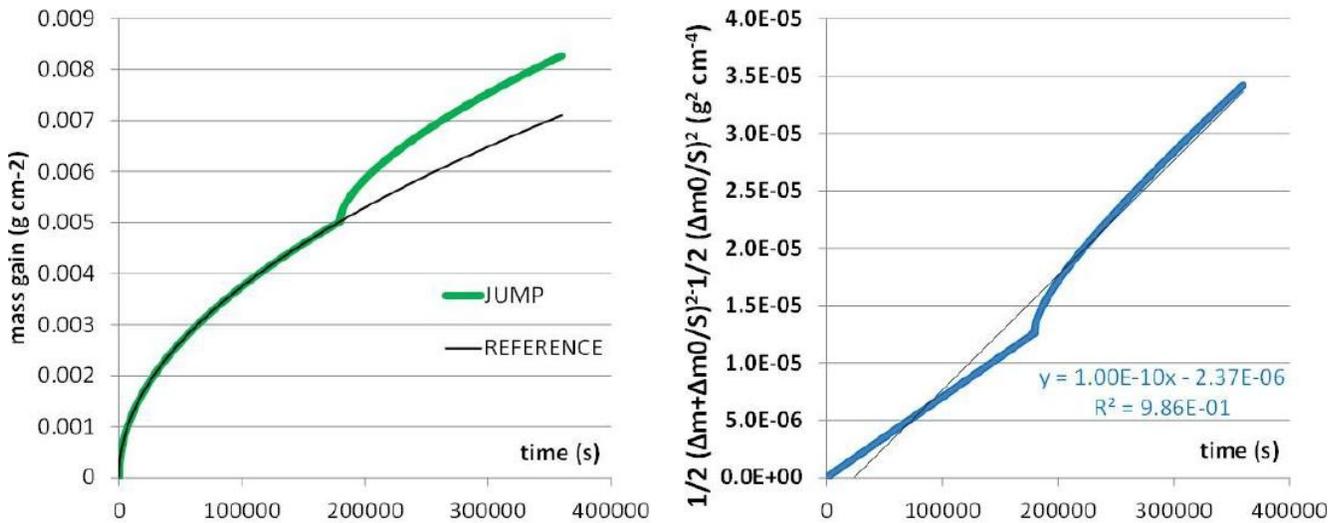


Figure 5 : The mathematical parabolic curve affected by an oxide scale detachment on 40% of the sample surface after 50 hours of isothermal oxidation (left; green thick curve plotted with the parabolic reference curve: black thin); K_p classically determined: $K_p = \text{slope} = 100 \times 10^{-12} \text{ g}^2 \text{ cm}^{-4} \text{ s}^{-1}$

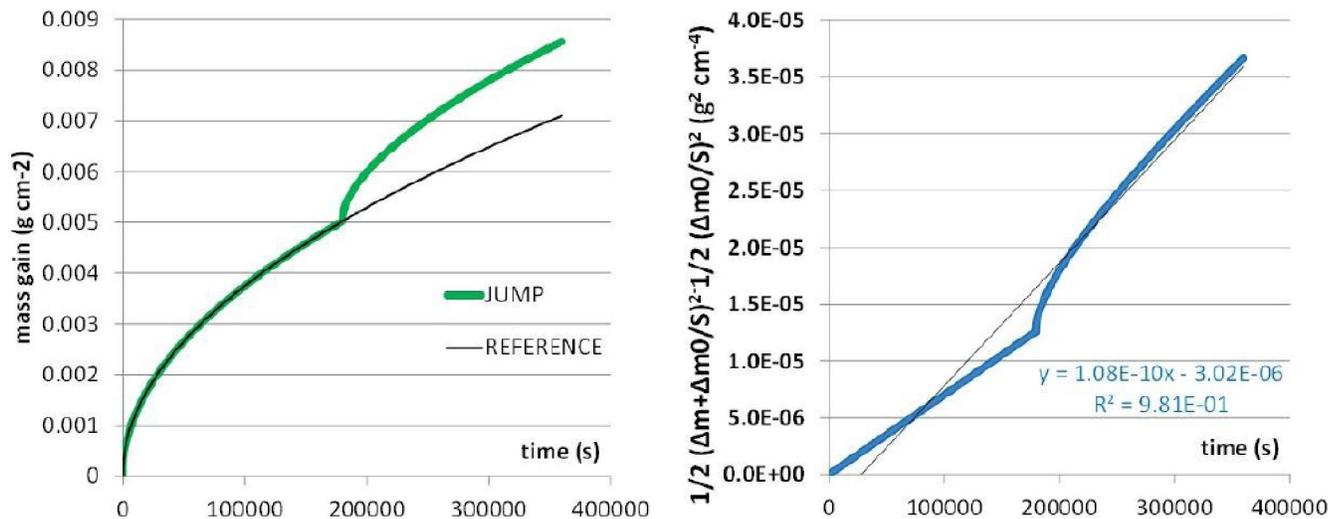


Figure 6 : The mathematical parabolic curve affected by an oxide scale detachment on 50% of the sample surface after 50 hours of isothermal oxidation (left; green thick curve plotted with the parabolic reference curve: black thin); K_p classically determined: $K_p = \text{slope} = 108 \times 10^{-12} \text{ g}^2 \text{ cm}^{-4} \text{ s}^{-1}$

curve, and in a second time the slope of the second part of the curves after the jump.

The obtained values were then compared to the real value $K_p = 70 \times 10^{-12} \text{ g}^2 \text{ cm}^{-4} \text{ s}^{-1}$ and their variations versus ξ or τ were studied.

RESULTS AND DISCUSSION

The mathematical curve which was considered as basis of the work is presented in the left side of Figure 1. It was plotted either by taking the mass gain achieved during the heating to the isothermal

stage temperature (e.g. 1200°C) into account “real” (thick green curve) or not “measured” (thin black curve). The K_p value injected in equations was $70 \times 10^{-12} \text{ g}^2 \text{ cm}^{-4} \text{ s}^{-1}$: this value was thereafter efficiently determined by the plot on the right side of the same figure.

The first case with an oxide scale detachment and consequently a jump in mass gain is presented in Figure 2: oxide scale detachment on 10% of the sample surface after 50 hours of isothermal oxidation. The jump is rather small thanks to the low value of surface fraction affected by the phenomenon. The

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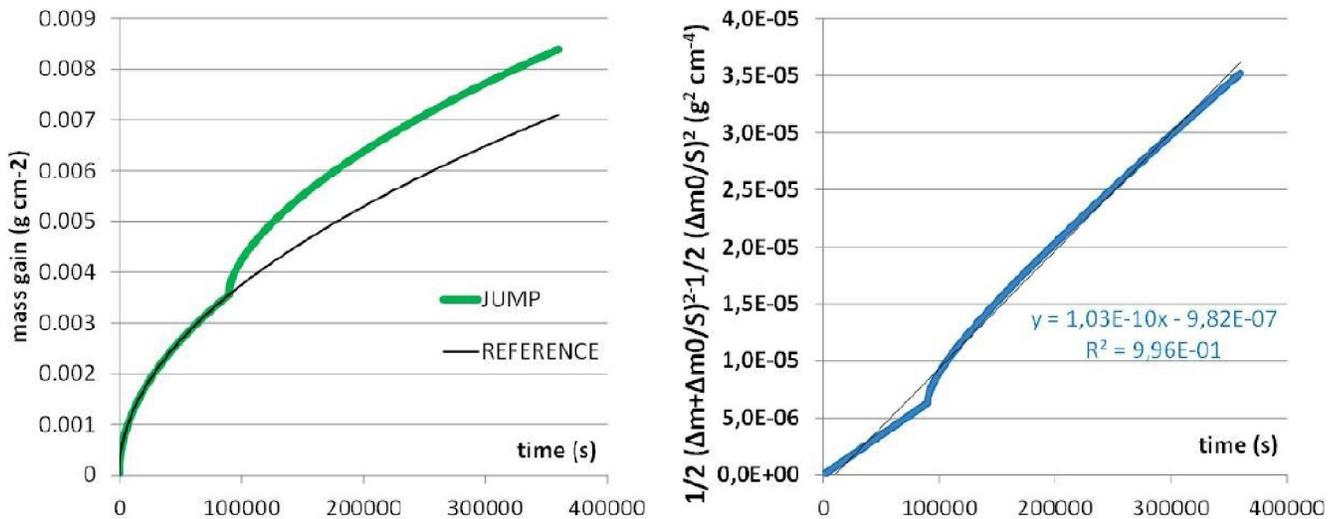


Figure 7 : The mathematical parabolic curve affected by an oxide scale detachment on 50% of the sample surface after 25 hours of isothermal oxidation (left; green thick curve plotted with the parabolic reference curve: black thin); K_p classically determined: $K_p = \text{slope} = 103 \times 10^{-12} \text{ g}^2 \text{ cm}^{-4} \text{ s}^{-1}$

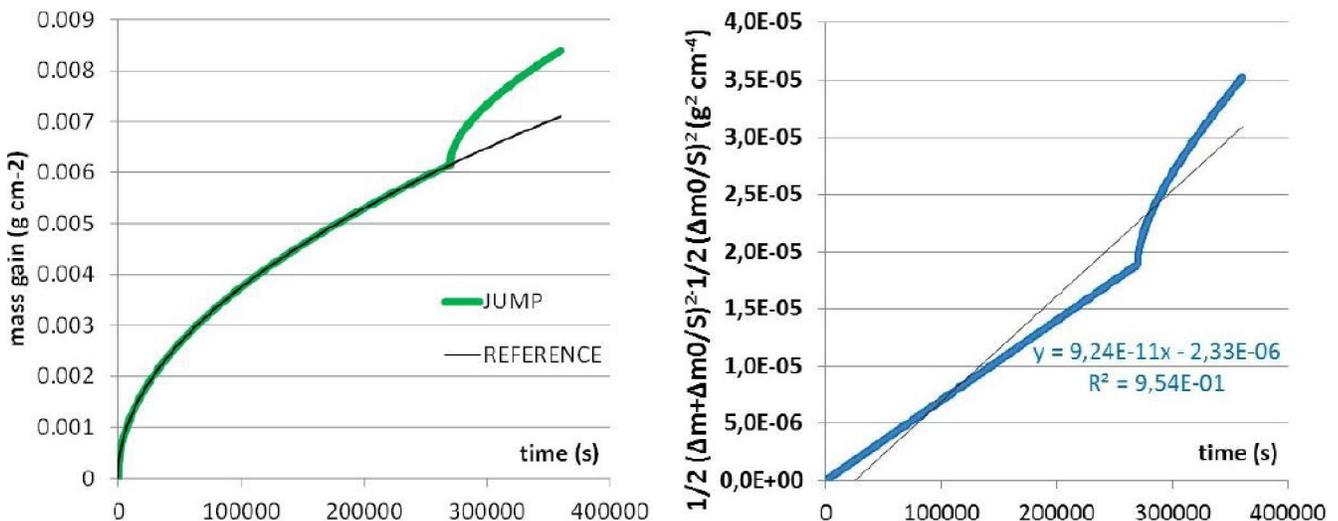


Figure 8 : The mathematical parabolic curve affected by an oxide scale detachment on 50% of the sample surface after 75 hours of isothermal oxidation (left; green thick curve plotted with the parabolic reference curve: black thin); K_p classically determined: $K_p = \text{slope} = 92.4 \times 10^{-12} \text{ g}^2 \text{ cm}^{-4} \text{ s}^{-1}$

K_p determination on the whole right-side curve leads to a value a little higher (about 10% more): $77.1 \times 10^{-12} \text{ g}^2 \text{ cm}^{-4} \text{ s}^{-1}$.

The second case (Figure 3), defined by an oxide scale detachment on 20% of the sample surface and after 50 hours of isothermal oxidation again, is characterized by a more marked jump, here too with a slope after jump higher than before. The K_p determination leads to $84.5 \times 10^{-12} \text{ g}^2 \text{ cm}^{-4} \text{ s}^{-1}$, as is to say a little higher than in the previous case. For 30% of the sample surface affected by oxide scale detachment after 50 hours of isothermal oxidation (Figure 4) this a value of K_p equal to $92.1 \times 10^{-12} \text{ g}^2$

$\text{cm}^{-4} \text{ s}^{-1}$ which was determined. For 40% of the sample surface affected by scale detachment $K_p = 100 \times 10^{-12} \text{ g}^2 \text{ cm}^{-4} \text{ s}^{-1}$ (Figure 5). Finally, for half surface, the higher fraction considered here, the K_p obtained by classical determination is $108 \times 10^{-12} \text{ g}^2 \text{ cm}^{-4} \text{ s}^{-1}$ (Figure 6). Thus, when the surface fraction of denuded alloy at $t=50$ hours increases, the average value determined on the whole curve may increase significantly. This is due to the slope of the last part of the curve {mass gain square versus time} which becomes higher and higher than the slope of the first part (before detachment) which remains constantly equal to the real value initially injected in the

equations ($70 \times 10^{-12} \text{ g}^2 \text{ cm}^{-4} \text{ s}^{-1}$). Indeed the slope of the last parts of the curves are $78.3 \times 10^{-12} \text{ g}^2 \text{ cm}^{-4} \text{ s}^{-1}$ for $\xi=0.1$, $87.1 \times 10^{-12} \text{ g}^2 \text{ cm}^{-4} \text{ s}^{-1}$ for $\xi=0.2$, $96.2 \times 10^{-12} \text{ g}^2 \text{ cm}^{-4} \text{ s}^{-1}$ for $\xi=0.3$, $106 \times 10^{-12} \text{ g}^2 \text{ cm}^{-4} \text{ s}^{-1}$ for $\xi=0.4$ and $116 \times 10^{-12} \text{ g}^2 \text{ cm}^{-4} \text{ s}^{-1}$ for $\xi=0.5$.

By keeping ξ equal to 0.5 the instant τ was also taken equal to 25h (90,000 seconds) and to 75h (270,000 seconds). The obtained average Kp values are $103 \times 10^{-12} \text{ g}^2 \text{ cm}^{-4} \text{ s}^{-1}$ (and $94.8 \times 10^{-12} \text{ g}^2 \text{ cm}^{-4} \text{ s}^{-1}$ for only the last part of the curve, after scale detachment, Figure 7) and $92.4 \times 10^{-12} \text{ g}^2 \text{ cm}^{-4} \text{ s}^{-1}$ (and $138 \times 10^{-12} \text{ g}^2 \text{ cm}^{-4} \text{ s}^{-1}$ for only the last part of the curve, after scale detachment, Figure 8), respectively. All these values are higher than the real $K_p=70 \times 10^{-12} \text{ g}^2 \text{ cm}^{-4} \text{ s}^{-1}$.

General commentaries

Thus, the obtained values of Kp by classical determination from the whole (irregular) curve or from only the part after the jump due to the simulated oxide scale detachment, are not correct. They are all more or less higher the one initially injected in formula for plotting the different mass gain curves. Fortunately these incorrect values are pessimistic. But is much better to consider only the early parts of the curves, before jump, even if, in real cases, these parts often contain a part of transient oxidation, and thus may be themselves not really correct.

CONCLUSIONS

The occurrence of jumps in mass gain happening when the external oxide scales become locally bending under the increasing compressive growth stress, is problematic for accurate determination of the parabolic constant which is very useful for the assessment of long-time sustainability. To solve this

problem, which is more frequently met for chromia-forming alloys than for alumina-forming ones (higher Pilling-Bedworth coefficient for chromia, higher than 2 against just a little higher than 1 for alumina) but also which can be partly solved by the presence of yttrium or other active elements, only repeating tests until obtaining a sufficiently delayed first jump, and measuring the slope of only the first part before the first jump, can lead to an accurate value of Kp. Unfortunately this one is the intrinsic one, but its significance for long-time behavior is limited since oxide scale detachments, by the acceleration of mass gain (obviously depending on the surface fraction affected and the time at which this occurs) and thus the deterioration that they induce, logically take part too.

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).
- [8] Elodie Conrath; PhD thesis, University of lorraine (France, defense on 2nd February 2016), (2016).