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Beginning of oxidation during heating in the case of cast nickel based alloys containing carbides of chromium and/or tantalum

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ABSTRACT

The heating parts of thermogravimetry curves initially performed with alloys or superalloys for studying their behaviour in isothermal oxidation, can be easily corrected from the Archimede's thrust in order to examine how oxidation acts during the heating. This was done in this work for several cast nickel-based alloys, a binary Ni-30Cr, six ternary Ni-30Cr-(0.2 to 2.0)C and three quaternary alloys containing Ta, for the same heating rate. The temperatures at which oxidation induced mass gains high enough to be detectable were all higher than 800°C, but with a reproducibility which can depend on the presence of tantalum for example. The total mass gain obtained at the end of heating was also studied versus the chemical composition of the alloys. Tantalum enhances oxidation during heating.

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KEYWORDS

Nickel alloys;
Chromium carbides;
Tantalum carbides;
High temperature;
Oxidation at heating;
Archimede's thrust.

INTRODUCTION

When exposed to high temperatures in oxidizing atmospheres, metallic alloys undergo oxidation by gases, notably by oxygen in aerated gaseous mixtures^[1]. In real situation, the metallic pieces used in hot conditions are generally neither wholly at the same temperature, nor at a temperature constant versus time. Nevertheless, the kinetic of their oxidation is often specified in isothermal conditions, like during thermogravimetry tests, except in cycling oxidation tests for which the mass loss due to oxidation followed by oxide spallation is often the single result recorded. Thermogravimetry results are currently devoted to the specification of the

Wagner's^[2] constant K_p characterizing the parabolic kinetic of mass gain. But they can be moreover used, not only for studying oxide spallation^[3,4], but also for specifying the characteristics of initial oxidation of the metallic surface during heating.

The purpose of this paper is to study the mass gain measurements recorded during the heating part of thermogravimetry runs in the case of cast nickel-based alloys containing varied natures and amounts of carbides, in order to specify several parameters characterizing the beginning and the rate of mass gain during this transient oxidation step preceding the isothermal oxidation.

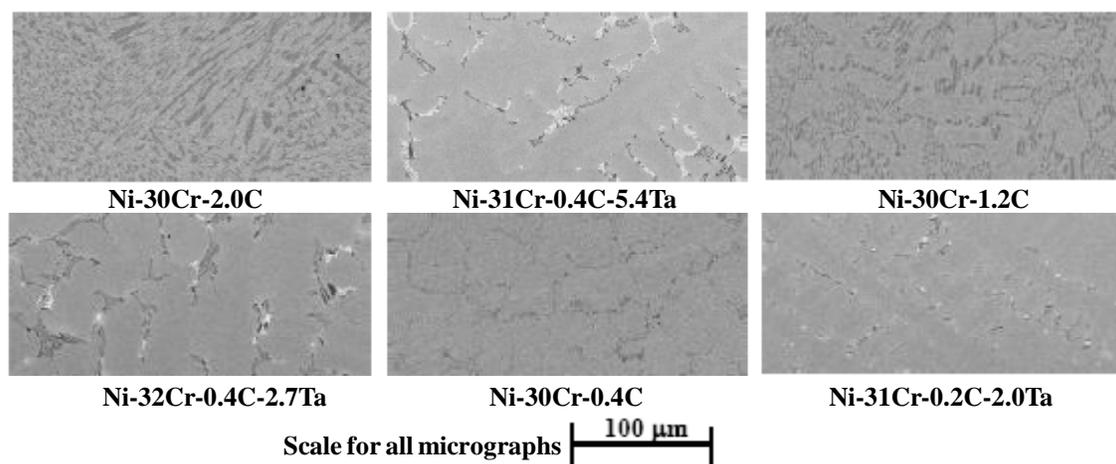


Figure 1: Micrographs of several alloys selected among the ones of this study (taken with a Philips XL30 scanning electron microscope, in back scattered electrons mode)

EXPERIMENTAL

Studied alloys

All the alloys considered in this work are based on nickel and contain seemingly the same quantity of chromium ($\approx 30\text{wt.}\%$ Cr). They differ from one another about their carbon content (binary Ni-30Cr or ternary Ni-30Cr-C with 0.2, 0.4, 0.8, 1.2, 1.6 and 2.0wt.% C)^[3], or about the presence, or not, of tantalum as a fourth element (Ni-31Cr-0.2C-2Ta, Ni-32Cr-0.4C-2.7Ta and Ni-31Cr-0.4C-5.4Ta, all contents in wt.%)^[4]. All these alloys were obtained by a foundry way: melting in inert atmosphere (pure argon, 300mbar) by high frequency induction (300kHz, CELES furnace) in a water-cooled copper crucible in which solidification was achieved too. The initial charge (100g) was composed of pure elements (Ni, Cr, Ta, C (graphite), all of a purity higher than 99.9wt.%). Their microstructures are reminded in figure 1, which displays, for a selection of these alloys, micrographs taken using a Scanning Electron Microscope (SEM, Philips model XL30) in Back Scattered Electrons mode (BSE). The binary alloy is single phased (FCC nickel with chromium in solid solution) and the ternary alloys contain in addition chromium carbides (appearing darker than matrix) the fraction of which increases with the carbon content. The quaternary alloys contain both chromium carbides and TaC carbides (whiter than matrix).

Thermogravimetry runs

Three samples were prepared from each alloy (par-

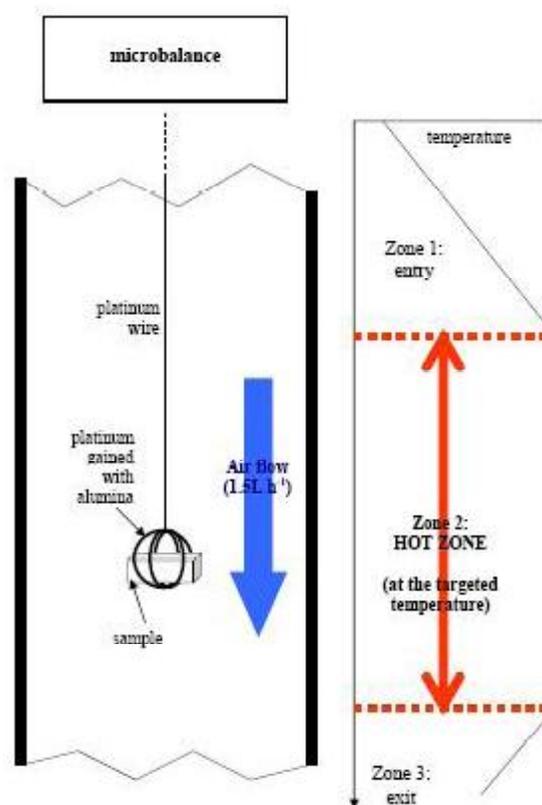


Figure 2: Scheme of the hot part of the thermobalance and of the different gradients of temperature

allepipeds of less than 0.4 cm^3 , polished with 1200-grit papers) and heated at 20 K min^{-1} from room temperature up to a high temperature equal to 1000, 1100 or 1200°C . When the maximum temperature was reached, the latter was maintained during 50 hours (binary and ternary alloys) or 100 hours (quaternary alloys) before cooling. The thermobalance which was

used for all tests was a Setaram TGA 92 one (a scheme of the hot part of such classical thermo balance is given in figure 2).

Treatment of mass gain measurements

After a short period during which the apparatus was reaching a thermal equilibrium (gas flow, studied metallic sample, platinum gained with alumina, platinum suspension on its whole length), the {sample + suspension} mass begins increasing continuously with time, even if temperature is not high enough for inducing significant oxidation. This is due to the decrease in Archimede's thrust due to the increase in temperature. Indeed, the state law of perfect gas written for two temperatures, a fixed one T_0 and a variable one T , assuming that P remains equal to 10^5 Pa independently on temperature (which is almost the case in the hot part of a thermobalance), allows obtaining the expression {Eq.1} giving the volume mass of air (ρ_{air}) at every temperature T from its value at another one T_0 (e.g. 20°C). The apparent mass (m_{app}) of the sample measured by the thermobalance is given from the real mass by deduction of the Archimede's thrust {Eq.2}. This second equation, written two times for two temperatures, a vari-

able one (T) and a fixed one (T_0), leads to {Eq.3}, and if the volume mass of air at T is replaced by its expression according to {Eq.1}, one arrives at {Eq.4} in which one can clearly see that, from 20°C for example, there is a positive difference of measured mass which increases with temperature.

$$\rho_{\text{air}}(T) = \rho_{\text{air}}(T_0) \times \left(\frac{T_0}{T}\right) \quad (1)$$

$$m_{\text{app}}(T) \times g = m \times g - \rho_{\text{air}}(T) \times V \times g \quad (2)$$

$$m_{\text{app}}(T) = m_{\text{app}}(T_0) + V \times (\rho_{\text{air}}(T_0) - \rho_{\text{air}}(T)) \quad (3)$$

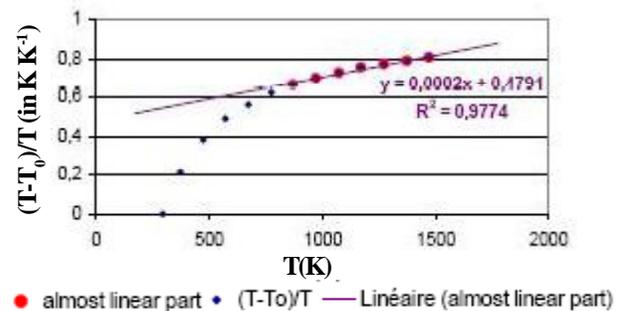


Figure 3: Evolution of $T-T_0/T$ versus T ; its linearity is evidenced over the range [873K 1473K], i.e. [600°C ; 1200°C]

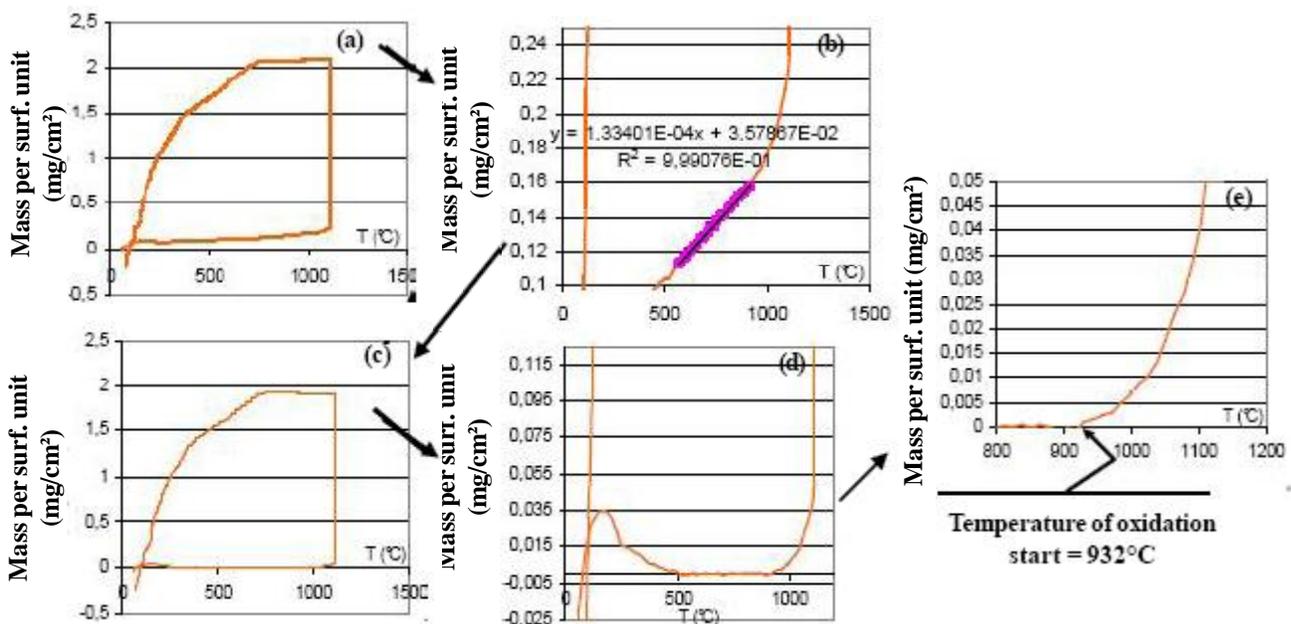


Figure 4: Example of treatment (here: binary Ni-30wt.%Cr alloy, targeted temp. 1100°C); (a) The whole mass gain curve plotted versus temperature, (b) Enlargement of the heating part where oxidation is obviously not yet started; determination of the equation for correction, (c) The whole curve after correction from mass variation due to the Archimede's thrust, (d) Enlargement of the heating part and visualization of the oxidation start, (e) Second enlargement and measurement of the temperature of oxidation start

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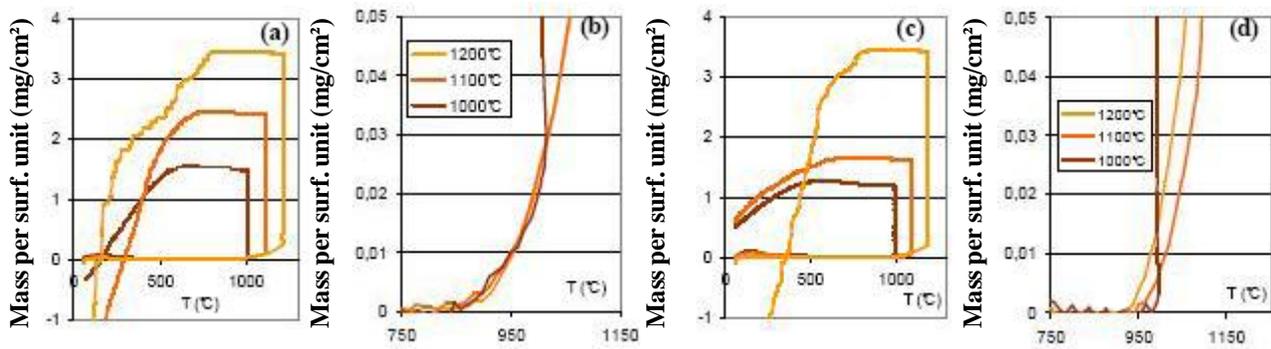


Figure 5: The mass gain curves for a Ni-30Cr-0.2C (a) (respectively Ni-30Cr-0.4C (c)) alloy for oxidation cycles at 1000, 1100 and 1200°C, with enlargement of the heating part around the temperatures at which oxidation starts (b, no significant differences) (resp. (d, small differences))

$$\begin{aligned}
 m_{\text{app}}(T) - m_{\text{app}}(T_0) &= V \times \rho_{\text{air}}(T_0) \times \left(1 - \frac{T_0}{T}\right) \\
 &= V \times \rho_{\text{air}}(T_0) \times \left(\frac{T - T_0}{T}\right) \quad (4)
 \end{aligned}$$

(V: sample+suspension volume, m: real mass of sample+suspension, g: gravity's constant (9.81 m s⁻²))

When T increases but is not yet far from 20°C, the (T - T₀)/T term varies rapidly, but when T has become high enough, the variation of (T - T₀) becomes preponderant by comparison to T alone. Then, (T - T₀)/T and m_{app}(T) - m_{app}(T₀), vary almost linearly. This becomes to be true when temperature is higher than about 600°C or 873K (figure 3).

Thus, above this level of temperature, if the thermogravimetry curve begins accelerating and quitting this linearity, this reveals a real mass gain, i.e. due to a beginning of oxidation with a significant combination of oxygen atoms with metallic elements belonging to the surface sample.

Figure 4 illustrates the method used in this work for characterizing the start of oxidation at heating. It begins with a preliminary correction of the mass gain curve, here plotted versus temperature (instead of time) for evidencing the successive phenomena^[3,4] (figure 4a): increase in mass gain at heating (apparent increase in mass due to the decrease in Archimede's thrust), acceleration of mass gain due to the starting oxidation, isothermal mass gain (mainly by parabolic oxidation), slow decrease in mass due to an increase in Archimede's thrust because of cooling, and finally rapid mass loss by oxide spallation.

In order to more efficiently evidence this loss of

linearity of mass gain, the equation of the linear part of the mass gain due to the decreasing Archimede's thrust, was determined (figure 4b). Thereafter this was subtracted to the measured mass gain (figure 4c). The new total mass gain curve presents a horizontal part staying at zero, where both the Archimede's thrust varied almost linearly and oxidation had not yet significantly started because of a temperature not yet become high enough (figure 4d). Finally, the end of this horizontal part can be zoomed in order to distinguish the start of mass gain due to real oxidation (figure 4e), and then determine the temperature of oxidation's beginning.

RESULTS AND DISCUSSION

Temperatures of oxidation start at heating

The procedure explained above allowed determining the temperatures of effective oxidation for all alloys, for the three tests performed until reaching 1000, 1100 or 1200°C. Two examples are given in figure 5, in which, for two alloys, the whole thermogravimetry curves plotted versus temperature for the three targeted maximal temperatures, are given on the left side (curves after correction from the Archimede's thrust, figures 5a and 5c), while zoomed views of the location where mass gain accelerated because of oxidation start are given on the right side (figures 5b and 5d). For some of the alloys, there was a good reproducibility of the position in temperature of the beginning of oxidation (figure 5b), what is not surprising since, of course, this temperature does not depend on the temperature at which the isothermal will be done thereafter. But, in other cases,

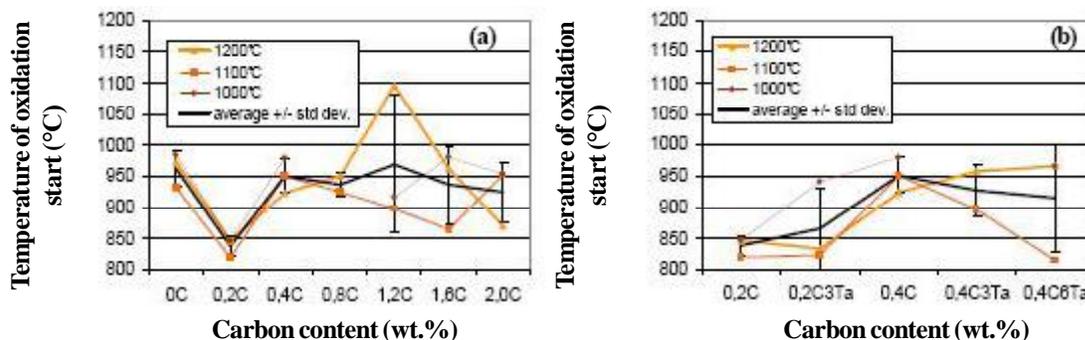


Figure 6: Temperature of oxidation start (i.e. at which mass gain begins to be significant): (a) Plotted versus the carbon content for the Ni-Cr-(C) alloys, (b) Effect of tantalum at constant carbon contents

there were more or less small differences between the three tests which were considered (figure 5d).

Thus, for each alloy, the three temperatures determined on the three curves were considered, with calculation of their average value and the standard deviation in order to get an interval of uncertainty. However, there were two exceptions (concerning the Ni-30Cr-0.8C alloy and the Ni-31Cr-0.4C-2.7Ta one, for the tests at 1000°C for both of them) in which the curious shape of the mass gain curve in its heating part revealed a possible problem during the tests (e.g. of suspension). The results are given in two graphs presented in figure 6. Figure 6a displays the evolution of oxidation's start temperature versus the carbon content for the binary/ternary alloys, for each of the three targeted temperatures for the isothermal stage (1000, 1100 and 1200°C), with the evolution of their average value \pm standard deviation (black line). Figure 6b presents the equivalent results in the case of the tantalum-containing alloys, with addition of the ternary alloys containing the same carbon contents for comparison.

It appears that oxidation really acts only above 800°C for all the alloys (the lowest temperature is 813°C, obtained with one of the curves corresponding to the Ni-31Cr-0.4C-5.4Ta alloy). But the interval of the temperatures of oxidation start is wide since the obtained values are spread up to 1096°C (one of the curves for Ni-30Cr-1.2C). The binary and ternary alloys with low carbon contents (≤ 0.8 wt.%) gave the best reproducibility, while more dispersed results were obtained for the highest carbon contents or when tantalum was present in the alloys. Unfortunately, this lack of reproducibility did not allow seeing whether there

was perhaps a specific evolution of the temperature of oxidation start versus either the carbon content, or the tantalum content. Nevertheless, one of the alloys seemed playing a particular role. Indeed, for the Ni-30Cr-0.2C alloy the temperature of oxidation start was systematically low with values varying only between 819 and 846°C. The addition of 2wt.% of tantalum introduced a dispersion of results, but with only a slight increase in the average value. Thus, the two alloys with 0.2wt.% C early began their oxidation during heating, significantly before all the other alloys.

Total mass gain during heating

On the curves corrected from the Archimede's thrust and plotted versus temperature, it was also possible to specify the total mass gain realized during the heating, more precisely between the temperature at which oxidation obviously started with a significant mass gain, and the beginning of the isothermal mass gain.

Another procedure was used in previous works to assess the mass gain by transient oxidation during heating, when thermogravimetry tests were run for at least three temperatures for a same alloy^[5]. This consisted in determining the slope of the initial linear part of the isothermal mass gain curve in the cases where the parabolic kinetic began after a short delay, or of the tangent to the parabolic mass gain curve at the early beginning of the isothermal stage when the mass gain began immediately according to the Wagner's law. This value, called linear constant of isothermal transient oxidation and noted K_i in these works^[5-8], were generally dependent on temperature and, more precisely, they followed an Arrhenius law. This type of representation (neperian logarithm of K_i plotted versus the reciprocal

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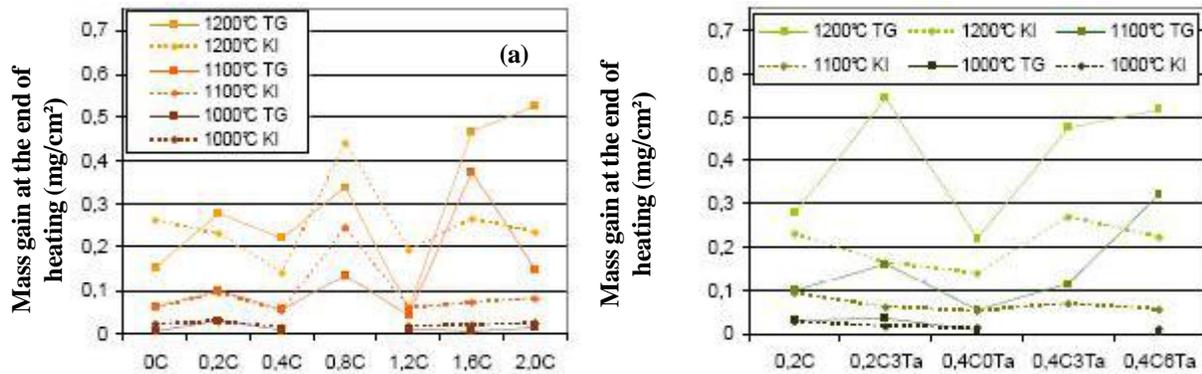


Figure 7: Mass gain at the end of heating, either according to thermogravimetry measurements corrected from Archimede's thrust (TG), or obtained by integration of the Arrhenius expression of the linear constant K_1 according to {Eq.6} (K_1)

absolute temperature $1/T$ (in K^{-1}) allowed determining an activation constant Q which allowed expressing K_1 as a function of temperature {Eq.5}, and thereafter estimating the mass gain realized during the heating {Eq.6}.

$$K_1 = K_{1_0} \cdot e^{\frac{-Q}{R \cdot T}} \quad (5)$$

$$\text{Mass gain (heating)} = K_{1_0} \cdot \int_{273K}^{T_{\text{test}}} e^{\frac{-Q}{R \cdot T(t)}} \cdot dt$$

$$\approx K_{1_0} \cdot \left(\sum_{n=1}^N e^{\frac{-Q}{R \cdot (273K + R_H \cdot n \cdot \Delta t)}} \right) \cdot \Delta t \quad (6)$$

in which K_{1_0} and Q are the Arrhenius constants of K_1 issued from the K_1 values obtained for the different test temperatures, R_H is the heating rate, Δt the recording time increment and N the number of recorded results during the heating ($N = (T_{\text{test}} - 243K) / (R_H \Delta t)$).

The two sets of values of the total mass gain at heating before isothermal oxidation are presented as graphs in figure 7: only for the Ni-Cr and Ni-Cr-C alloys in figure 7a, and, in figure 7b, for the Ni-Cr-C-Ta alloys, with addition of the tantalum-free ternary alloys containing the same carbon amounts, for comparison. In contrast with figure 6, the values obtained with the same alloy for the three temperatures of isothermal oxidation must be separated from one another, since the higher the test temperature, the higher the total mass gain during heating, logically. This is effectively verified since the curves bounding the points for 1200°C are above the curves for 1100°C, and the latter above the curves for 1000°C. Concerning the two ways of deter-

mination of the total mass gain during heating, there are often significant differences. Considering the three test temperatures together for a same alloy (1000, 1100 and 1200°C), the two sets of values are globally consistent for the ternary alloys with low and medium carbon contents (between 0.2 and 1.2C). This is a little less true for the binary alloy and for the Ni-30Cr-0.8C one. In contrast, it is really worse for the ternary alloys with 1.6 and 2.0wt.%C, as well as for the three tantalum-containing alloys.

Concerning the Ni-Cr(-C) alloys, this is in accordance with the quality of the alignment of the three points in the Arrhenius plot^[7,8]. Indeed, the very good or excellent alignment of the points $\{1/T; \ln(K_1)\}$ obtained in these previous works for the low carbon ternary alloys led to good values for the activation energy Q , which thereafter allowed estimating with accuracy the total mass gain during the whole heating. Inversely, the bad alignment of the points existing for the three values of $\ln(K_1)$ plotted versus $1/T$ in the case of the two carbon-richest ternary alloys^[7], led to a value of Q which was only good enough to obtain a sufficiently accurate value of mass gain existing just before parabolic oxidation acted, to determine the parabolic constant K_p with accuracy. Here the values of mass gain during heating estimated by this way is, in contrast, worse than the direct measurement on the thermogravimetry curves corrected from the Archimede's thrust. About the three alloys containing tantalum, despite of the excellent alignment of the points $\{1/T; \ln(K_1)\}$ in Arrhenius plot^[6], the values of the activation energy for K_1 led here to mass gain at the end of heating which are often different from what

can be directly measured in the thermogravimetry curves corrected from the Archimede's thrust.

If one considers only the mass gains at heating end directly measured on the latter thermogravimetry curves, no systematic relation seems existing with the carbon content in the tantalum-free alloys (figure 7a). In contrast, it appears that these mass gains tend to be higher for the alloys with tantalum than for the alloys without tantalum, for a same carbon content (figure 7b).

General commentaries

When an alloy with a surface initially metallic is heated, oxidation takes place more or less early. One can remind that this begins with nucleation of oxides points, followed by lateral growth of oxides from these nuclei along the surface and thickening perpendicularly to the surface. This leads to a discontinuous layer of oxide, the growth of which tends to be fast because not yet governed by diffusion of ions through the oxides already existing, but the kinetic of which is still limited because of the temperature which is not yet very high. When temperature is high enough, oxidation becomes really fast, for the two precedent reasons together, with consequently a mass gain which is important enough to be detected and measured by a microbalance.

This can be done by considering the Archimede's thrust decrease, the linearity of which was demonstrated for temperatures high enough, but the value of which was not directly used to subtract to the measured mass gain. Indeed, if the volume of the sample and a part of the volume of its suspension were in the hot zone (the temperature of which is well known thanks to a thermocouple), the other part of this suspension is in a zone of lower temperatures (as illustrated in figure 2), and taking into account the variation of apparent mass of these "colder" parts during heating cannot be really done. This is the reason why it was here preferable to simply measure the slope of the linear part of the mass gain curve at heating, and subtract it from the whole curve. One can remark that, if this was important to do that for a good accuracy for the determination of both the temperature of the beginning of significant mass gain by oxidation and the total mass gain during heating, such correction should be not really useful for the other part of the thermogravimetry curve where temperature also varies, as is to say the cooling part. Indeed, if one wishes

studying the rate of oxide spallation for example, the mass variations induced are too important or fast to be significantly modified by the Archimede's thrust variations.

Here, for the studied alloys, the mass gain due to oxidation during heating occurred at temperatures more or less higher than 800°C. In some cases, almost the same value of oxidation start's temperature was found for the three tests for the same alloy, but this reproducibility was not found in other cases. Such differences can be attributed to differences of surface reactivity due to difference of microstructure orientation or of microstructure fineness between two samples of a same alloy. Indeed, it was already observed that these microstructure parameters can influence the behaviour of oxidation at high temperature^[9]. The presence of tantalum seemed also being another source of dispersion: this can be attributed both to the randomly dispersed TaC carbides among the chromium carbides in the interdendritic spaces (figure 1) and to the behaviour of this element in oxidation (Ta is more easily oxidable than Cr and it can accelerate the nucleation of oxide). In addition, the presence of tantalum obviously led to higher mass gains achieved at the end of heating. Here too this can be due to the high reactivity of this element in high temperature oxidation, which probably led to an amount of oxides of tantalum (Ta_2O_5) or chromium and tantalum together ($CrTaO_4$) at the end of heating, higher than the mass of NiO and/or Cr_2O_3 in the case of the binary and ternary alloys. On the contrary, a possible effect of carbon, which however varied over a wide range (0 to 2wt.%), was not really observed (except the surprising behaviour of the alloys containing 0.2wt.%C with or without Ta, which remains to be explained).

The direct measurement of these mass gains at the end of heating, on the thermogravimetry curves corrected from the Archimede's thrust, appears more efficient than integration from the Arrhenius expression of the linear constants K_1 . This can be due to the hypothesis which must be done in the latter case (a single phenomenon, thermally activated over the whole temperature range between the lowest ones and the targeted ones), and which is sometimes not true. One can think that determining by this direct measurement the mass of oxygen adsorbed, then the thickness of the pre-existing

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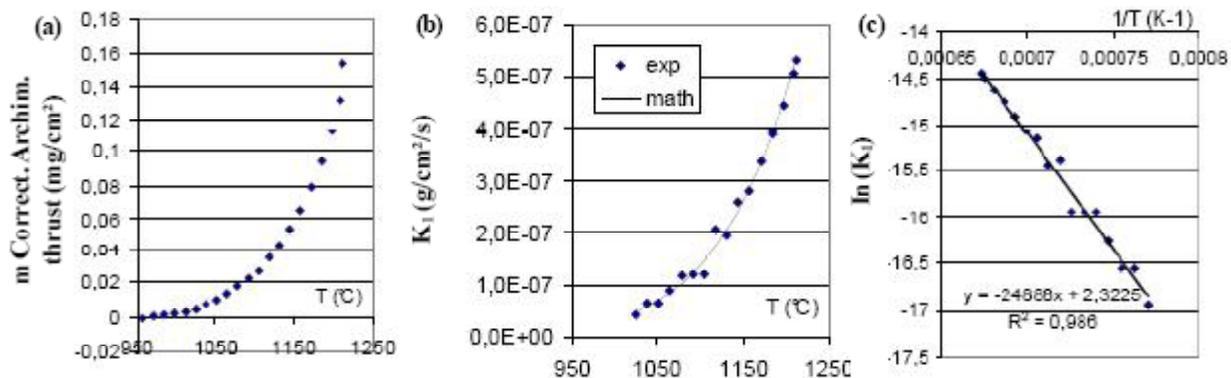


Figure 8: Determination of K_1 versus temperature at the end of heating for the binary Ni-30Cr alloy heated up to 12000C; (a) Enlargement of the thermogravimetry curve at the end of heating; (b) Plot of $K_1(T) = (dm/dt)_T(T)$ versus temperature at the end of heating (.exp.) and with {Eq.10} determined in c (.math.); (c) Arrhenius plot of $\ln(K_1)$ versus $1/T$ in order to determine the constant value (2.3225) and the slope (-24888K), from which the values of K_{10} (10.2g/cm²/s) and Q (207kJ/mol)

oxide, before isothermal oxidation can be more efficient for preparing the calculation of the parabolic constant.

To finish, one can remark that it finally appears that it is not necessary, for an alloy, to perform several thermogravimetry runs at three (or more) temperatures sufficiently far from one another (e.g. 1000, 1100 and 1200°C) to examine how the linear constant varies with temperature and, furthermore, to specify the values of the parameters of its Arrhenius expression. Indeed, if one considers again the thermogravimetry measurements at heating after their correction from the Archimede's thrust, it is possible to determine K_1 at each step of increase in temperature, by applying {Eq.7}:

$$K_1(T) = \left(\frac{dm}{dt} \right)_T(T) \approx \frac{m[T(t + \Delta t)] - m[T(t)]}{\Delta t} \quad (7)$$

where T is the temperature at the time t and $m[T(t)]$ the mass gain (corrected from the Archimede's thrust) at this temperature T (or at this time t), and Δt the time step of record (here 40s).

In the case of the binary Ni-30wt.%Cr and the targeted temperature 1200°C (figure 8), the mass gain m corrected from Archimede's thrust begins increasing from about 1000°C (figure 8a). The calculation of K_1 at each step leads to the experimental ("exp") successive values of $K_1(T)$ plotted versus temperature in figure 8b. Thereafter, plotting $\ln(K_1(T))$ versus $1/T$ (K⁻¹) leads to the equation of the regression straight line, given in figure 8c, which allows calculating the two Arrhenius parameters: the activation energy Q ({Eq.8}) and the

multiplying coefficient K_{10} ({Eq.9}):

$$Q = (-R \times \text{slope}) = (-8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times (-24888 \text{ K})) = 207 \text{ kJ mol}^{-1} \quad (8)$$

$$K_{10} = \exp(\text{ordinate at origin}) = \exp(2.3225) = 10.2 \text{ g cm}^{-2} \text{ s}^{-1} \quad (9)$$

Thereafter, using these two values in {Eq.10}, one can plot the mathematical curve ("math") which can be compared to the experimental one ("exp") in figure 8b. The fit appears excellent.

$$K_1(T) = K_{10} \times e^{\left(\frac{-Q}{R \times (T(^{\circ}\text{C}) + 273.15\text{K})} \right)} \quad (10)$$

In a future work it will be interesting to study the reproducibility of these results (Arrhenius parameters in the equation giving $K_1(T)$), and to compare these Arrhenius expressions for different alloys (e.g. different contents in carbon or tantalum in nickel-based alloys) or for different microstructure textures (e.g. dendritic orientation or fineness).

CONCLUSIONS

Exploiting the heating parts of thermogravimetric measurements before isothermal oxidation at high temperature allowed here revealing different behaviours of initial oxidation, when the first parts of oxide nucleate and grow. It is rather easy to correct the thermogravimetry curve from the apparent variation of mass gain due to the decreasing Archimede's thrust, and get curves on which the beginning of oxidation can be evidenced. If tantalum seems playing an important role in this oxidation

during heating for these nickel-based alloys, it could be interesting to also specify the role of other active elements. It could be also interesting to systematically study the effects of other parameters as the microstructure texture or the heating rate.

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