



Materials Science

An Indian Journal

Full Paper

MSAIJ, 11(8), 2014 [273-281]

Effect of a high hafnium content on the high temperature oxidation of chromium-rich cast alloys. Part 3: Oxidation at heating of Ni-based alloys

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ABSTRACT

Hafnium is added to high temperature alloys to improve their resistance against hot oxidation. Despite that this element is often present only in small quantities (around 1 wt.%), it plays an efficient role. It is possible to add it in much higher quantities, for example in carbon-containing alloys in which Hf can be trapped in carbides. It is therefore interesting to see whether its beneficial effect on high temperature oxidation is stronger or remains the same or, on the contrary, or whether too much hafnium becomes detrimental for oxidation resistance. Here, cast chromium-rich nickel-based alloys containing particularly high Hf quantities were subjected to oxidation at 1000 and 1100°C in dry air for 46 hours, similarly to what was earlier done for similar alloys but at 1200°C. The heating parts of the obtained thermogravimetric curves were exploited after correction from air buoyancy variation. The temperatures of oxidation start, the total mass gain during heating, the instantaneous linear constant versus temperature and the transient oxidation linear constant were determined and analysed versus the contents of the alloys in carbon and in hafnium. This led to interesting observations, notably concerning the oxidation start temperature and its dependence on the chemical composition of these nickel-based alloys.

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KEYWORDS

Nickel-based alloys;
High hafnium contents;
High temperature;
Transient oxidation;
Thermogravimetry.

INTRODUCTION

The most often high temperature alloys in service must resist mechanical solicitations (e.g. creep) but also chemical aggressions^[1]. Concerning the second point good resistance against high temperature oxidation can be achieved by enriching alloys in chromium, aluminium or silicon in order to favour the formation of continuous protective oxide scales which significantly decrease the oxidation rate^[2]. These three elements, added in sev-

eral tens of weight percents, are the most important elements for this objective. This is true in isothermal service conditions, but in real applications temperature often varies and a serious problem existing besides the oxidation rate itself is the possible loss of protective oxide scale which leads, for the alloy, to the formation of a new scale, this itself inducing an impoverishment in Cr, Al or Si respectively.

To limit such phenomenon, rare earth or active elements are added to alloys to improve the adherence of

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the scales over the alloys (as well as other aspects of high temperature oxidation resistance). One of these elements is hafnium, which is added in some nickel-based alloys. One can thus find about 1wt.% of Hf (or less) for example in NiFe-based^[3], Ni-based^[4,5] or NiAl-based^[6-8] alloys. In contrast several weight percents in hafnium, such as 4 or 5wt.%, are much more encountered among the common alloys and superalloys for high temperature uses. This is precisely the reason why here one capitalized on the availability of nickel-based alloys especially rich in hafnium^[9] to examine how high Hf contents may influence some aspects of the behaviour in oxidation of nickel-based chromium-rich alloys at 1000 and 1100°C.

EXPERIMENTAL DETAILS

The alloys of the study

The nickel-based alloys considered in this work were designed by choosing high chromium content (25wt.%Cr) to allow a chromia-forming behaviour for all alloys, and by choosing two levels of carbon contents (0.25 and 0.50wt.%) to obtain significant populations of carbides in the microstructures. The chosen hafnium contents, 3.7 and 5.6wt.% Hf, were much higher than the usual Hf contents which can be encountered in more common alloys and superalloys. The alloys which will be studied here were previously synthesized by foundry. The liquid alloys were obtained by melting pure elements together, and solidified in the metallic crucible of the used furnace. Their as-cast microstructures have been already characterized^[9] while their oxidation behaviours were investigated at 1200°C^[10,11]. Some of these latter oxidation results will be added to the ones of the present work to allow studying over [1000, 1200°C].

The names and chemical compositions (obtained by Energy Dispersive Spectrometry) of the five alloys considered for the present study are:

- “Ni-25Cr-0.25C-3.72Hf”: 25.70wt.% Cr and 4.40wt.% Hf (Co: bal., C: not measured)
- “Ni-25Cr-0.50C-3.72Hf”: 25.57wt.% Cr and 4.79wt.% Hf (Co: bal., C: not measured)
- “Ni-25Cr-0.50C-5.58Hf”: 25.32wt.% Cr and 6.64wt.% Hf (Co: bal., C: not measured)

- “Ni-25Cr-0.25C”: 23.79wt.% Cr (Co: bal., C: not measured)
- “Ni-25Cr-0.50C”: 22.74wt.% Cr (Co: bal., C: not measured)

The as-cast microstructures of these five alloys, which are reminded in Figure 0, were previously described in the initial work^[9]. To summarize one can say that all alloys present a dendritic matrix composed of an austenitic nickel-chromium solid solution, and of carbides. These

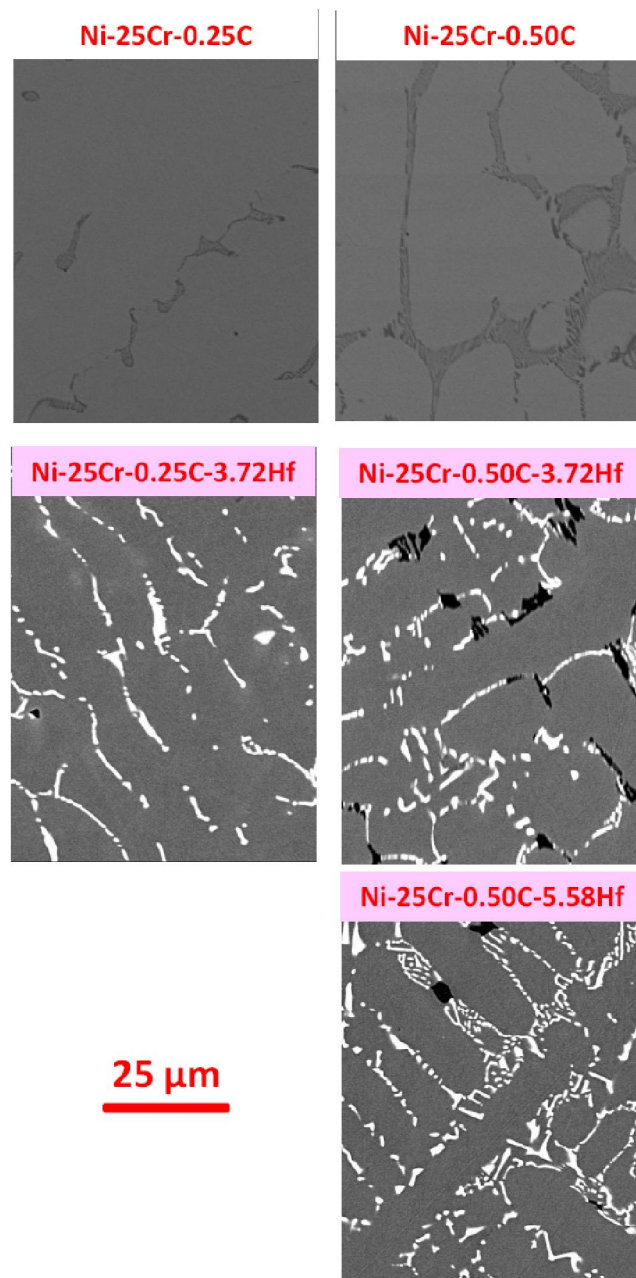


Figure 0 : Micrographs illustrating the as-cast microstructures of the five studied alloys (Scanning Electron Microscope JEOL JSM-6010LA, Back Scattered Electrons mode)

ones are hafnium carbides and sometimes chromium carbides in the as-cast Hf-containing alloys. The as-cast Hf-free alloys only contain chromium carbides.

Preparation of the samples for the thermogravimetry tests

Cutting the ingots near their centres allowed obtaining parallelepiped samples for the oxidation tests. These samples were ground all around with 1200-grade SiC paper after having smoothed the edges and the corners with a 240-grade SiC paper. The oxidation tests were performed with a thermobalance (Setaram TG92), in a continuous flow of dry artificial air (80% N₂-20% O₂).

The thermal cycle was composed of:

- a heating at 20°C min⁻¹,
- an isothermal (1000 or 1100°C)-stage during 46 hours
- a cooling at -5°C min⁻¹

For the exploitations of the heating parts of the mass gain files one applied the procedures described in a previous work [12]:

- plot of the mass gains versus temperature (and not time as usually done) to obtain an equation thereafter used to correct the mass gains from the varia-

tions of air buoyancy,

- determination of the temperature at which oxidation has become significant enough to allow a detectable mass gain,
- study of the evolution of the kinetic linear constant between the oxidation start temperature and the stage temperature,
- analysis of the temperature-dependence of this linear constant in the Arrhenius scheme and determination of the corresponding activation energy,
- determination of the total mass gain achieved during heating.

In addition, the mass gain rate existing just after having reached the isothermal stage temperature was determined. The slope of the tangent straight line (mass gain represented versus time) was determined to obtain a value of the linear constant of transient oxidation (during the isothermal linear oxidation if any, or at the early start of the parabolic regime).

RESULTS AND DISCUSSION

The {mass gain versus temperature}-curves during heating

The mass gain recorded during heating are plotted

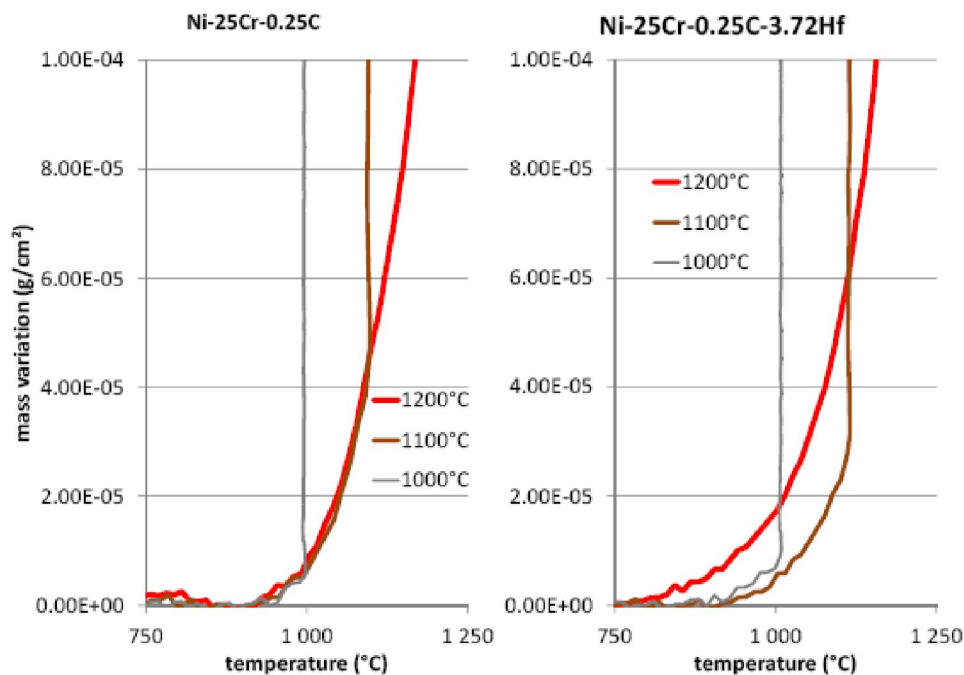


Figure 1: Mass gain curves during heating plotted versus temperature for determination of the temperatures of oxidation start (criterion: detection of mass gain with the used thermo-balance) and for the total mass gain during the whole heating; here: the two 0.25wt.%C-containing alloys

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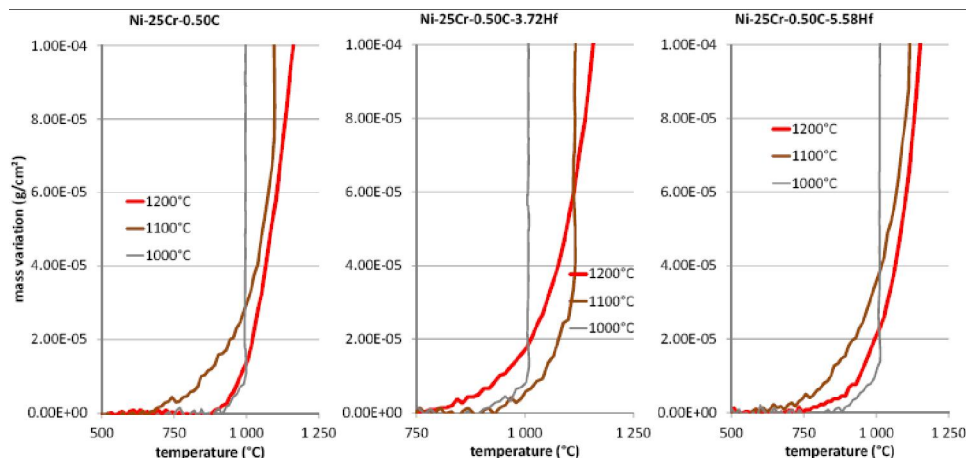


Figure 2 : Mass gain curves during heating plotted versus temperature for determination of the temperatures of oxidation start (criterion: detection of mass gain with the used thermo-balance) and for the total mass gain during the whole heating; here: the three 0.50wt.% C-containing alloys

versus temperature in Figure 1 for the {0.25C}-alloy (left) and the {0.25C-3.72Hf}-alloy (right). For each alloy the graphs containing the curves for the tests corresponding to the isothermal stage temperatures 1000 and 1100°C (this work) are enriched with the curves previously obtained for a stage temperature of 1200°C^[10]. The oxidation during heating of the {0.25C}-alloy presents a good reproducibility for the common part of the three curves ($T < 1000^\circ\text{C}$). It is not the case for the {0.25C-3.72Hf}-alloy. Indeed the sample destined to the 1200°C isothermal oxidation test has obviously started to oxidize sooner than the ones destined to isothermal oxidation at 1000 and 1100°C (and – maybe consequently – faster than them) despite that the test conditions (e.g. heating rate, air flow...) were the same for the three samples in the heating part below 1000°C.

Figure 2 shows the curves of the same type but obtained for the {0.50C}-alloy (left), the {0.50C-3.72Hf}-alloy (middle) and the {0.50C-5.58Hf}-alloy (right). This time the lack of reproducibility concerns the three alloys, Hf-free or Hf-containing. The common parts ($T < 1000^\circ\text{C}$) of the three heating curves are never superposed, whatever the alloy.

Temperatures of oxidation start

For each of the alloys, the temperatures at which the mass gain becomes to be significant enough to be detectable by the used thermo-balance, can be specified on the previous graphs presented in Figure 1 and Figure 2. The results are presented in the histogram shown in Figure 3.

Here too one finds again that cumulating the results obtained for a same alloy give an idea on their reproducibility and then their representativeness. As suspected above by looking to the heating parts of curves, the temperature of oxidation start is not really the same for a single alloy and for the three targeted stage temperatures. The three values are close to one another only in the cases of the {0.25C}-alloy and of the {0.25C-3.72Hf}-alloy. This is not the case for the three other alloys for which the results are very scattered. How-

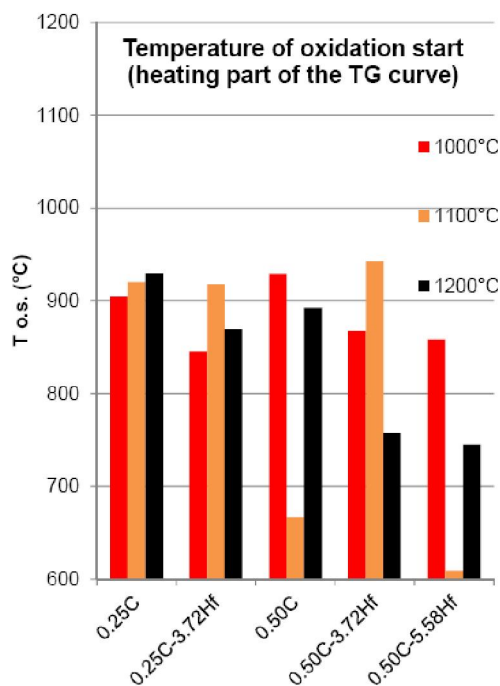


Figure 3: Histogram presenting the values of oxidation start temperature for the five alloys when heated up to 1000 and 1100°C (this study), and also 1200°C (previous study^[10])

ever it seems that oxidation starts to be detectable sooner for the three {0.50C}-alloys than for the {0.25C}-alloys but without reproducibility. It is possible that an interdendritic carbides network composed of many HfC carbides – as is to say of carbides formed with an element particularly oxidable – favours a better exposition of this elements to oxidation, then an earlier start of oxidation during heating. However the results' dispersion shows, in this hypothesis, that the carbides network is not developed enough to well establish this effect.

Total mass gain during heating

The total mass gains achieved during the whole heating are shown in the histogram presented in Figure 4 (top: full scale, bottom: enlargement for better seeing the low values). The heating up to 1000°C seemingly leads to heating mass gains which increases with the carbon content and with the presence of hafnium and its contents. The effect of the carbon content remains for heating up to 1100°C (increase of the heating mass gain with the carbon content) while the presence of hafnium, on the contrary, tends to lower this heating mass gain (except for the {0.50C, 5.58Hf}-containing alloy for which the heating mass gain is the highest among the five alloys. For heating up to 1200°C the heating mass gain tends decreasing when the carbon content increases in absence of hafnium while it is the inverse effect which is seen in presence of hafnium in the alloy.

Instantaneous linear constant versus temperature

During the whole heating and from the temperature at which the oxidation has become to be detected an instantaneous linear constant of mass gain, noted $K_i(T)$, has been calculated for each temperature step by deriving the mass gain by time (by dividing by the time step the mass gain difference between two successive records). As previously seen for iron-based alloys^[13], this instantaneous constant more or less obeyed an Arrhenius law, notably in the high temperature part of heating (low values of $1/K$), as proven by the good linearity of $\ln(K_i(T))$ versus $1/K$. This allowed determining values of activation energies. These ones are graphically presented in Figure 5. The values corresponding to the heating up to the 1000°C-isothermal

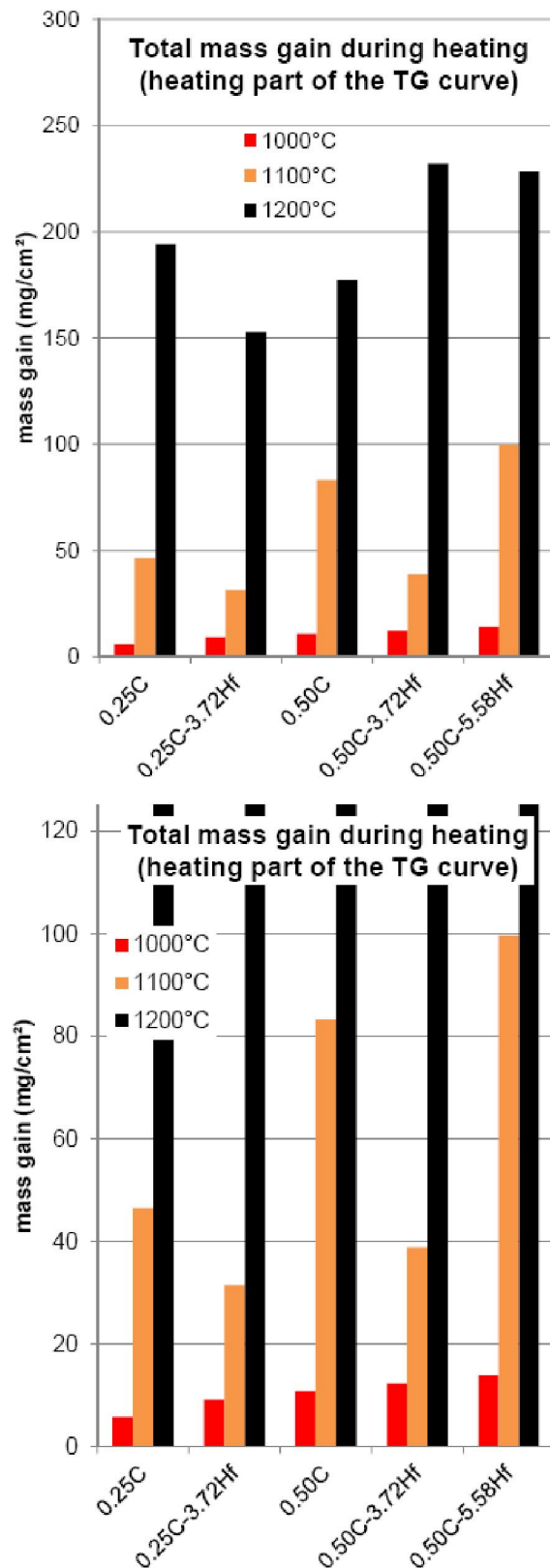


Figure 4 : Histogram presenting the values of total mass gain at the end of heating, for the five alloys when heated up to 1000 and 1100°C (this study), and also 1200°C (previous study⁽¹⁰⁾): full scale (top) and zoomed (bottom)

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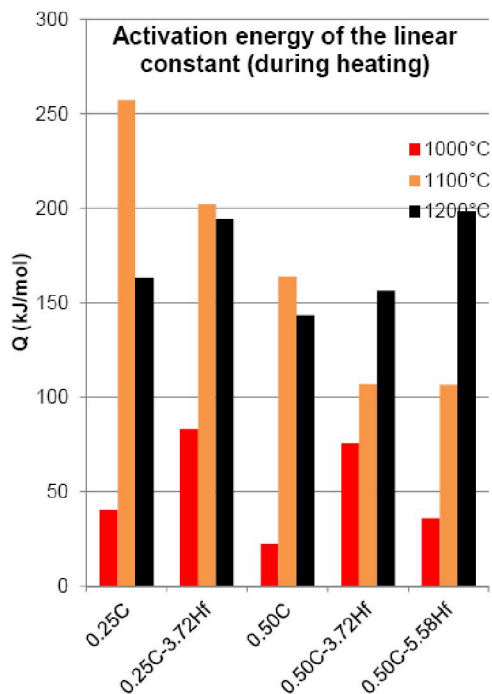
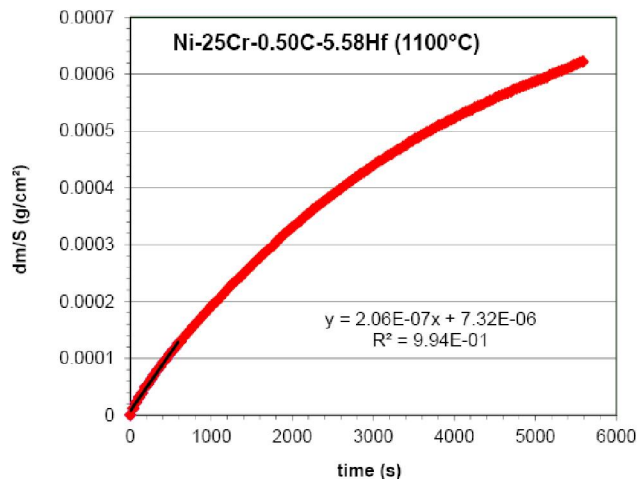


Figure 5 : Histogram presenting the values of the corresponding activation energies obtained for the five alloys when heated up to 1000 and 1100°C (this study), and also 1200°C (previous study^[10])



$$K_l(T_{stage}) = \frac{\partial \left(\frac{\Delta m}{S} \right)}{\partial t} \text{ at } t = t_{stage \text{ start}}$$

Figure 6 : Determination of the linear constant characterizing the linear transient oxidation at the beginning of the isothermal stage

stages are scattered but also rather low: one can wonder if the temperature range is wide enough to really allow such determination. The activation energies obtained for heating up to 1100 and 1200°C seems evaluate more clearly versus the alloy's chemical composi-

tion... but unfortunately in inverse directions depending of the maximal temperature. Indeed, for heating up to 1100°C the activation energy seems decreasing when the carbon content increases and when the hafnium content increases. For heating to 1200°C, it is exactly the contrary: the highest the carbon content or the highest the hafnium content, the highest the activation energy.

Linear constant representing the transient mass gain rate at the isothermal stage beginning

The final kinetic characteristic of the mass gain during heating is the rate at which the mass gain continues its increase in the first times of the isothermal stage. Without correction from air buoyancy variation (temperature has now become constant), the mass gain files present a more or less long first part linear versus time. The slope of the curve at this isothermal stage beginning was then determined and gave a value to the linear constant K_l (which depends on the stage temperature). An example of determination is given in Figure 6 (case of the Ni-25Cr-0.50C-5.58Hf alloy arrived at the stage temperature of 1100°C).

The dependence of K_l versus the stage temperature is graphically presented in Figure 7 for the two {0.25C}-containing alloys (top: Ni-25Cr-0.25C, bottom: Ni-25Cr-0.25C-3.72Hf) and in Figure 8 for the three {0.50C}-containing alloys (top: Ni-25Cr-0.50C, middle: Ni-25Cr-0.50C-3.72Hf, bottom: Ni-25Cr-0.50C-5.58Hf). One can see first that the three points are very well aligned in two cases (Ni-25Cr-0.25CHf and Ni-25Cr-0.50C-5.58Hf). This is less true in the cases of the Ni-25Cr-0.50C and Ni-25Cr-0.50C-3.72Hf alloys, while the alignment is the worst for the Ni-25Cr-0.50C-3.72Hf alloy. The activation energies are of 200-250kJ/mol for the first cited alloys (good alignment) and lower than 200kJ/mol for the other ones: around 180kJ/mol and even 130kJ/mol for the alloy with the less aligned points (value not representative). Generally these activation energies are higher than the ones determined above for the instantaneous linear constant during heating.

General commentaries

The heating parts of the thermogravimetry curves may be of interest for better understand the behavior in

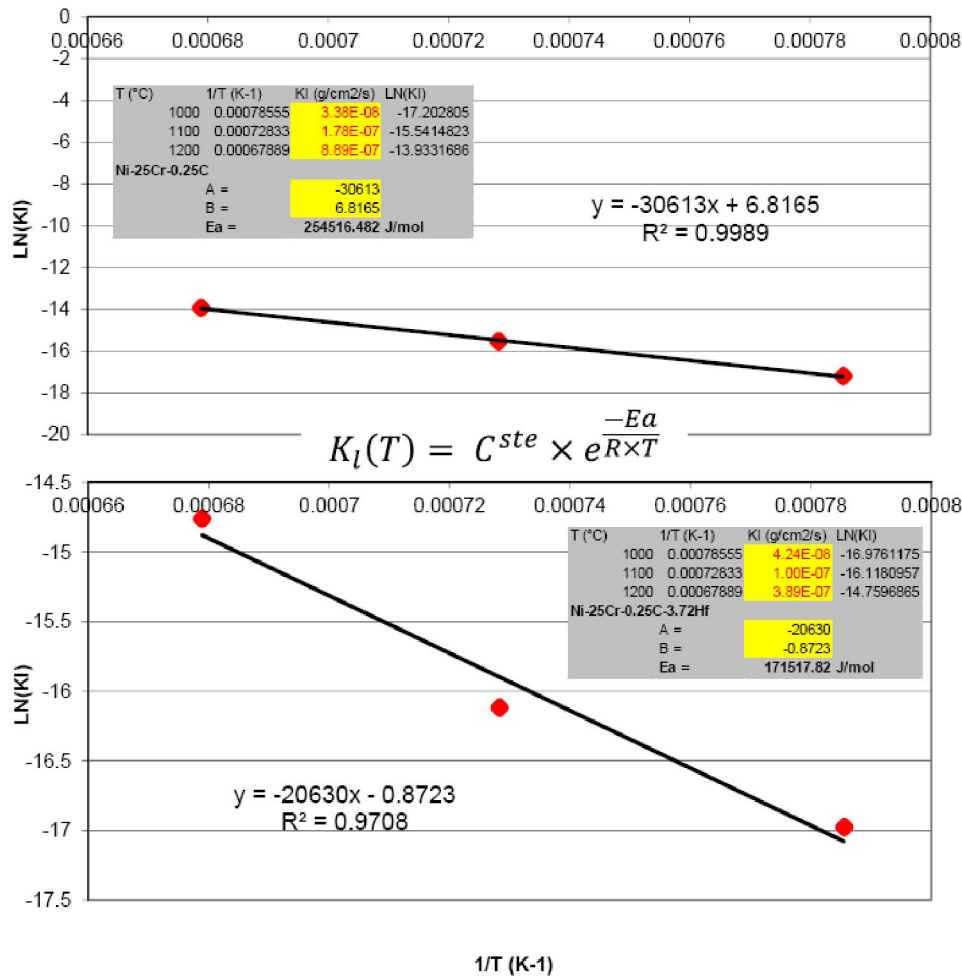


Figure 7 : Arrhenius plot and values of the K_l linear constants; value of the corresponding activation energy (for the two {0.25wt.%C}-containing alloys)

oxidation at high temperature of alloys, and to complete the characterization of the influence of their chemical compositions of microstructures in this field. Here this started by the correction of the mass gain files from the air buoyancy variations which may lead to virtual mass variations and then to bad interpretations. After having proceeded to this correction the first results obtained concerned the temperature at which appears a detectable mass variation due to oxidation and only oxidation. It appeared first that an higher carbon content tends to sooner oxidation start during heating, as is to say to a lower temperature. This was seen first for the two Hf-free alloys (oxidation start temperature lower for 0.50C than for 0.25C), and second for the two low Hf alloys (oxidation start temperature lower for the 0.50C-3.72Hf alloy than for 0.25C-3.72Hf one). This can be explained by a denser carbide network for 0.50C which emerges on surface and then which better expose the most

oxidable elements Cr or Hf to oxidation. The oxidation appears sooner during heating also when the alloy contains hafnium (oxidation start temperature lower for the 0.25C-3.72Hf alloy than for the 0.25C one, and for the 0.50C-3.72Hf alloy than for the 0.50C one): this can be attributed to a slightly more developed interdendritic carbide network in the second case (despite the same carbon content) resulting from the strongest carbide-former character of hafnium by comparison with chromium. But it can be also due to a most oxidable character of hafnium, always in comparison to chromium. This suspected higher tendency to oxidize of hafnium by comparison with chromium may be also responsible of the highest total mass gains achieved during heating up to 1000°C and up to 1200°C. However, the opposite observations were done for heating up to 1100°C. The results concerning the activation energies of the instantaneous linear constant as well as

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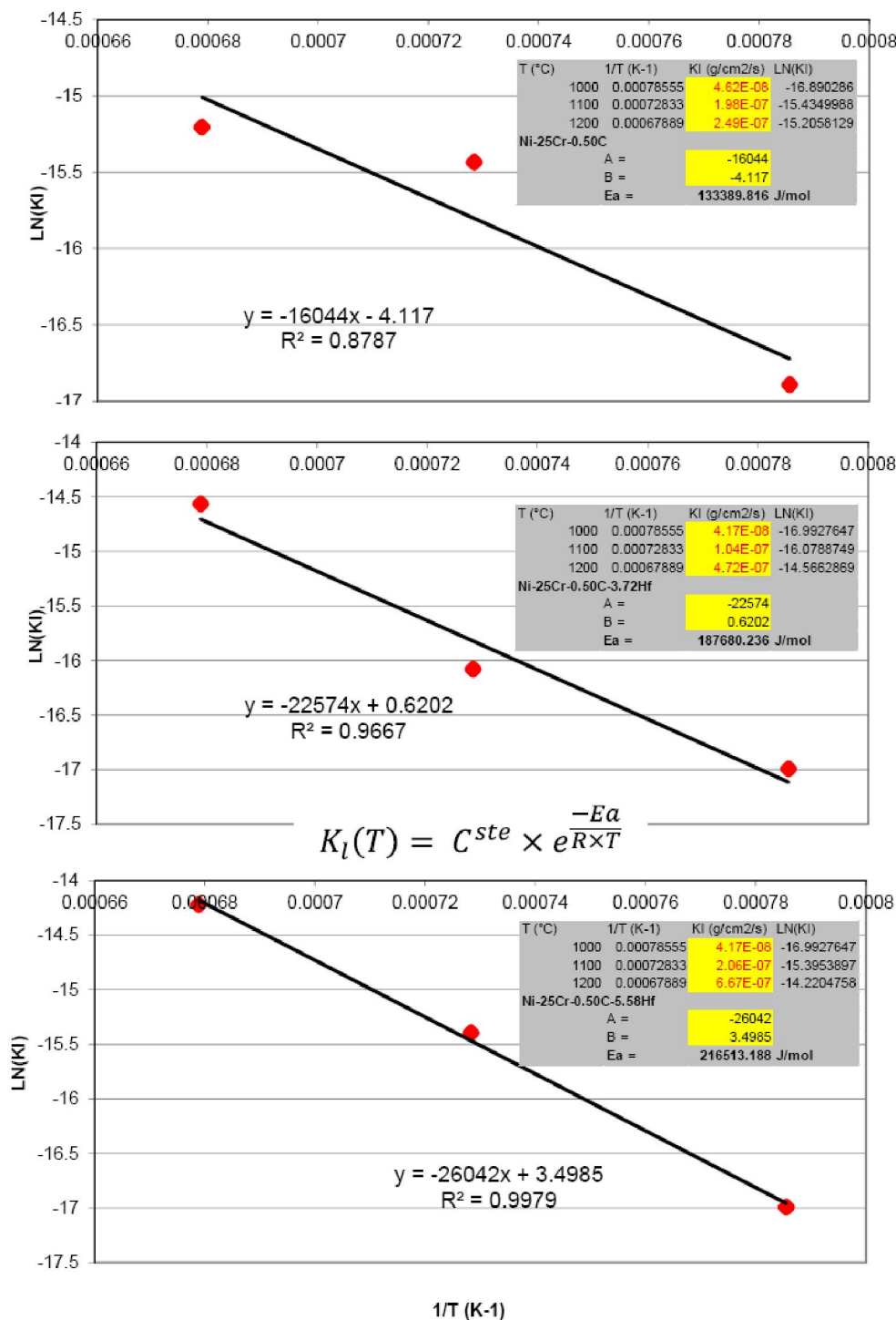


Figure 8 : Arrhenius plot and values of the K_l linear constants; value of the corresponding activation energy (for the three {0.50wt.%C}-containing alloys)

the transient oxidation linear constant at the beginning of the isothermal stage, and notably the dependence on the chemical composition of the alloy, are less clear and then more difficult to interpret. However it is remarkable that these constants seem rather well obeying an Arrhenius law.

CONCLUSIONS

The exploitation of the heating parts of the thermogravimetry curves, the later ones being more devoted to the study of the isothermal oxidation of the

alloys, is rarely done although this may lead to interesting data. The results obtained in this work for ternary Ni-25Cr-xC and Hf-rich quaternary Ni-25Cr-xC-yHf were interesting but unfortunately not always exploitable because a dispersion which was sometimes too wide to allow good conditions of analyze and clear interpretations. However first interesting observations were done and explained, notably concerning the oxidation start temperature. This is of importance since these phenomena are the preliminary ones and they may more or less influence also the following isothermal oxidation. This study of the effect of particularly high contents in hafnium in chromia-forming nickel-based alloys on the start of oxidation and the oxidation during heating will be followed by the analyze of the effect of these high hafnium concentrations on the isothermal oxidation and one the behavior of the externally formed oxide scales during cooling^[14].

REFERENCES

- [1] M.J.Donachie, S.J.Donachie; ‘Superalloys: A Technical Guide’ (2nd Edition), ASM International, Materials Park, (2002).
- [2] J.Young; ‘High temperature oxidation and corrosion of metals’, Elsevier, Amsterdam, (2008).
- [3] W.S.Lee, G.M.Kim; Han’guk Pusik Hakhoechi, **23(3)**, 170 (1994).
- [4] W.S.Lee, G.M.Kim; Han’guk Pusik Hakhoechi, **24(2)**, 124 (1995).
- [5] N.A.Lysenko, V.VKudin, V.G.Klochikhin, I.Tsivirkol; Metal Science and Heat Treatment, **41(1-2)**, 32 (1999).
- [6] C.Xu, J.Guo, F.Yang; Jinshu Xuebao, **37(8)**, 857 (2001).
- [7] J.T.Guo, C.M.Xu; Oxidation of Metals, **58(5/6)**, 457 (2002).
- [8] Z.Wang, L.Zhou, J.Guo, Y.Liang, Z.Hu; Cailiao Yanjiu Xurbao, **24(6)**, 585 (2010).
- [9] P.Berthod; Materials Science: An Indian Journal, **9(9)**, 359 (2013).
- [10] E.Conrath, P.Berthod; Materials Science: An Indian Journal, **10(1)**, 30 (2013).
- [11] P.Berthod, E.Conrath; Materials Science: An Indian Journal, **10(6)**, 240 (2014).
- [12] P.Berthod; The Open Corrosion Journal, **4**, 1 (2011).
- [13] E.Conrath, P.Berthod; Materials Science: An Indian Journal, submitted.
- [14] E.Conrath, P.Berthod; Materials Science: An Indian Journal, to be submitted.