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Effect of a high hafnium content on the high temperature oxidation of chromium-rich cast alloys. Part 5 : Oxidation at heating of co-based alloys

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ABSTRACT

After the nickel-based alloys and the iron-based alloys, this is here the case of the cobalt-based alloys which is examined concerning the effect of unusually high hafnium contents on the oxidation during heating up to 1000 or 1100°C. The thermogravimetric tests were done in air for 50 hours and the obtained mass gain files exploited in their heating part. A correction from the air buoyancy variation was realized to obtain mas gain curves suitable for analyses. The studied parameters were the temperature of oxidation start, the total mass gain during heating, the instantaneous linear constant versus temperature, the linear constant representing the pre-parabolic transient oxidation, and finally the corresponding activation energies. These characteristics describing the behaviour of the alloys in oxidation during heating were all studied with regards to the contents of the alloys in carbon and in hafnium. Generally the results were not very clear. However interesting observations were done, for example concerning the total mass gain achieved during heating.

KEYWORDS

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

INTRODUCTION

Some superalloys contain hafnium in their chemical compositions[1]. This rather expensive element, which is added in small quantities (around 1wt.% and the most often lower), brings the alloys a better resistance against oxidation at high temperature[2], in terms of oxidation rate and especially of resistance against oxide spallation in thermal cycling. In particular, hafnium may be encountered in some cobalt-based superalloys, as well as in some cobalt-based coatings[3-6]. More hafnium may be added in cobalt-based alloys without promoting possible metallurgical instabilities when carbon is also present in sufficient quantities Indeed, hafnium is a very strong carbide-former element and, even if another carbide-former element as chromium is present in much higher quantity " for example with a content 30wt.% " all the carbon atoms are trapped in HfC carbides[7].

Knowing the beneficial effect of hafnium when added in low quantities, one can think that new improvements may be obtained by enriching the alloys in this element beyond 3 wt.%. But it is also possible that too high contents in this reactive element may inversely appear as detrimental. It is the purpose of this work to discover, in the case of cobalt alloys rich in chromium, the effect of very high hafnium quantities in hafnium on the high temperature oxidation behaviour of Co-based alloys. In this first part this is the oxidation during heating up to either 1000 or 1100°C, which will be characterized by thermogravimetry tests, in the case of three Hf-rich 25wt.%-containing cobalt-based alloys and two Hf-free alloys with the same chromium and carbon contents.

EXPERIMENTAL DETAILS

The alloys of the study

The cobalt-based alloys of the study, which contain a rather high chromium content to promote a chromia-forming behaviour (25wt.%Cr for all of them) as well as two levels of carbon contents (0.25 and 0.50wt.%), designed with hafnium contents significantly higher than usually. The Hf contents of these alloys are 3.7 and 7.4wt.%Hf, as is to say much more than the most common Hf contents usually added to alloys. These alloys were already earlier elaborated by foundry from pure elements in order to explore the microstructures which may be obtained as-cast for chromium-rich cobalt alloys containing simultaneously carbon and high Hf quantities[8]. Some aspects of the oxidation behaviour of these alloys were also previously studied at 1200°C[9,10]. The results which were then obtained at 1200°C will be, for some of them, recalled to be added to the results of the present work. This will allow extending the analysis from 1000 to 1200°C. The five alloys are the following ones (name, followed by the chemical composition obtained by Energy Dispersive Spectrometry):

- "Co-25Cr-0.25C-3.72Hf": 25.51wt.% Cr and 3.81wt.%Hf (Co: bal., C: not measured)
- "Co-25Cr-0.50C-3.72Hf": 25.59wt.% Cr and 3.88wt.%Hf (Co: bal., C: not measured)
- "Co-25Cr-0.50C-7.44Hf": 25.82wt.% Cr and 8.78wt.%Hf (Co: bal., C: not measured)
- "Co-25Cr-0.25C": 24.22wt.% Cr (Co: bal., C: not measured)
- "Co-25Cr-0.50C": 23.79wt.% Cr (Co: bal., C: not measured)

Their microstructures in the as-cast condition, previously described[8], are reminded in Figure 1 by some SEM/BSE micrographs (SEM: Scanning Electron Microscope; BSE: Back Scattered Electrons mode) in which the HfC carbides appear white and the chromium carbides dark.

Shortly:

- the matrixes of the two Hf-free alloys are dendritic, and in their interdendritic spaces more or less chromium carbides are present (rare in the 0.25wt.%C-containing alloy, more present in the 0.25wt.%C-containing one),
- the matrixes of the three Hf-containing alloys are also dendritic and they contain script-like eutectic HfC carbides in their interdendritic spaces;
- the Co-25Cr-0.25C-3.72Hf alloy and the Co-25Cr-0.50C-7.44Hf one additionally contain pre-eutectic polygonal HfC carbides while the Co-25Cr-0.50C-3.72Hf alloy contains some rare chromium carbides.

Preparation of the samples for the thermogravimetry tests

The five ingots have been cut in the centres of the ingots in order to obtain parallelepiped samples. These ones were ground with SiC papers of 240-grade to smooth their edges and their corners. Thereafter the samples were wholly polished with SiC paper of 1200-grade. The thermogravimetry runs were performed with a thermobalance (Setaram TG92), in a continuous flow of dry artificial air (80%N_2-20%O_2).

The thermal cycle which was applied can be described by the following three phases:

- heating at 20°C min^{-1},
- isothermal (1000 or 1100°C)-stage during 50 hours
- cooling at -5°C min^{-1}

The heating parts of the mass gain files were treated and exploited according to procedures which were earlier described[11]. Initially, the mass gains were plotted versus temperature (and not time as usually done). This allowed obtaining an equation which was thereafter used to correct the mass gains from the air buoyancy variations. The corrected mass gains were then plotted again and analyzed to obtain the following data:

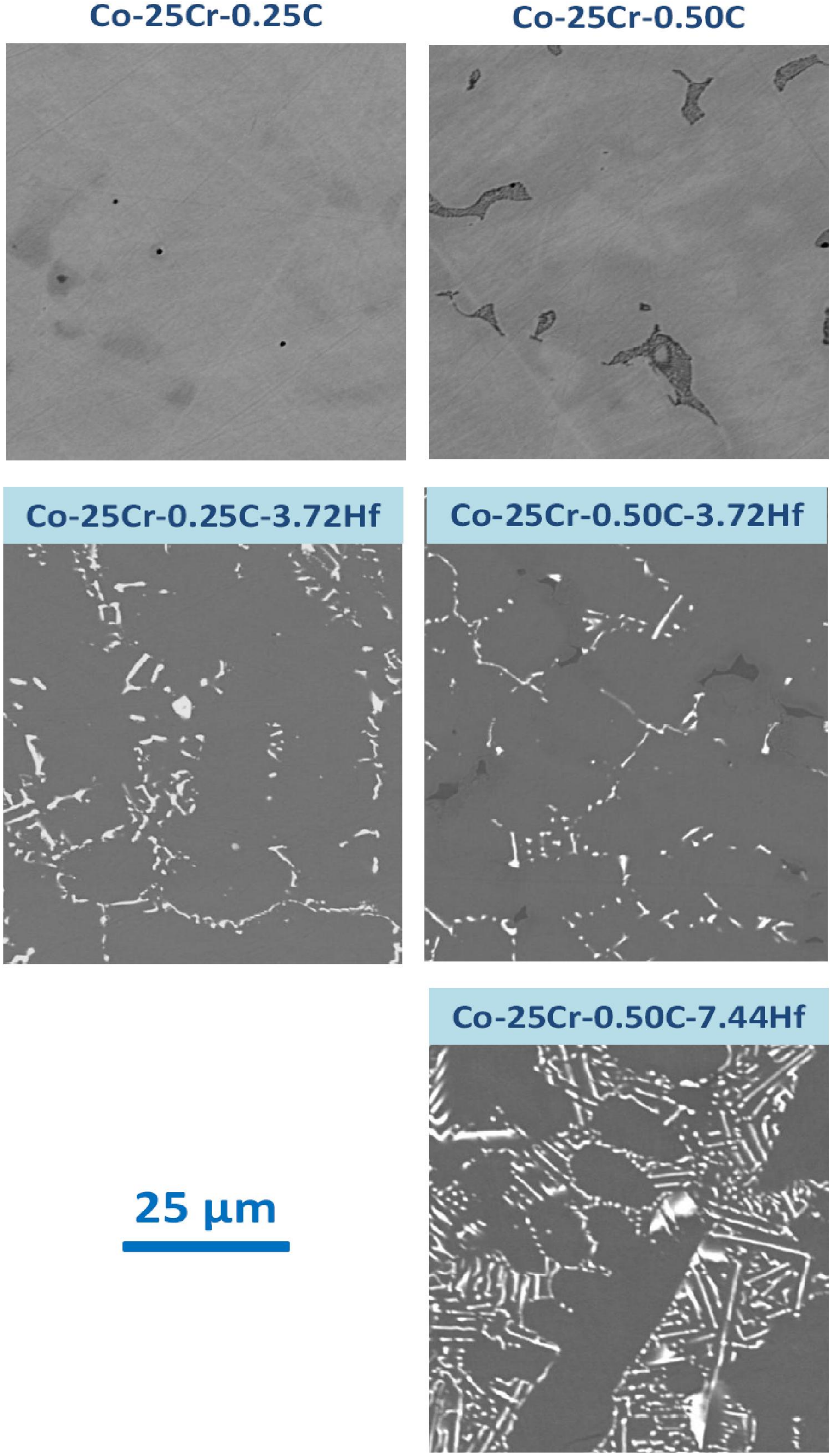


Figure 1 : Micrographs illustrating the as-cast microstructures of the five studied alloys (Scanning Electron Microscope JEOL JSM-6010LA, Back Scattered Electrons mode)

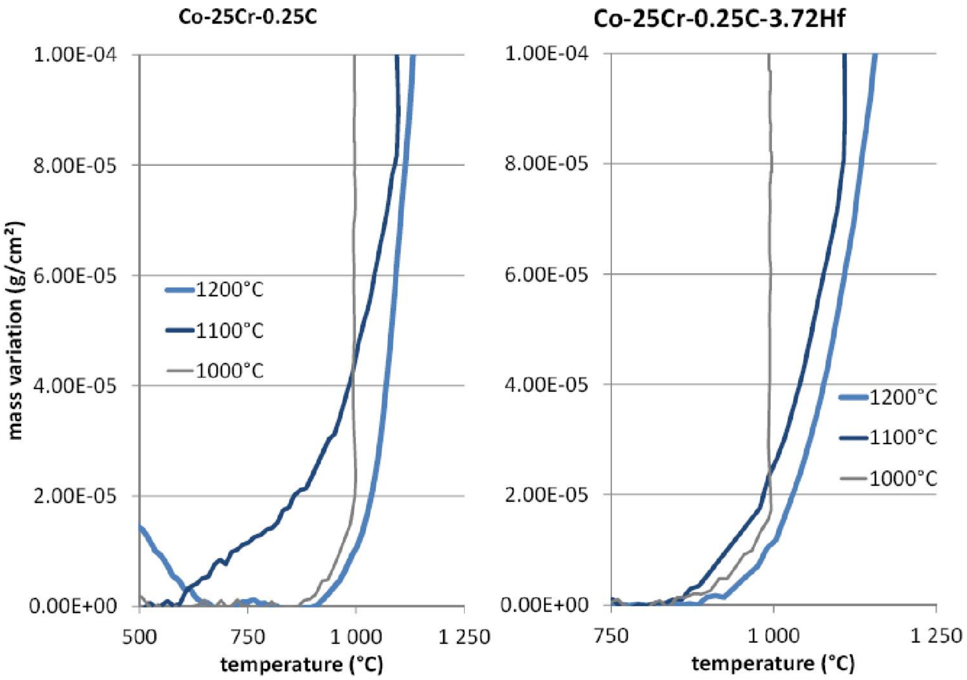


Figure 2 : Mass gain curves during heating plotted versus temperature for determination of the temperatures of oxidation start (criterion: detection of mass gain with the used thermo-balance) and for the total mass gain during the whole heating; here: the two 0.25wt.%C-containing alloys

- the temperature at which oxidation began to be fast enough to lead to a detectable mass gain
- the successive values of the linear constant at each recording step between the oxidation start temperature and the stage temperature; analysis in the Arrhenius plot and determination of the corresponding activation energy
- the total mass gain which was achieved during the whole heating.

Additionally, one also took in consideration the mass gain rate existing just after that temperature reached the isothermal stage temperature: 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 it exists, or at the early beginning of the parabolic regime).

RESULTS AND DISCUSSION

The {mass gain versus temperature}-curves during heating

The mass gain recorded during heating and plotted versus temperature are displayed in Figure 2 for the {0.25C}-alloy (left hand) and the {0.25C-3.72Hf}-alloy (right hand), in each case for the three tests for which the temperature stage are 1000 and 1100°C (this work) and also 1200°C[9]. There is obsviously a lack of reproducibility for the Co-25Cr-0.25C alloy since, if two of the curves show an oxidation start at almost the same temperature, the oxidation start temperature shown by the third curve (stage temperature of 1100°C) is significantly bellow.

The curves of the same type but obtained for the {0.50C}-alloy (left hand), the {0.50C-3.72Hf}-alloy (middle) and the {0.50C-5.58Hf}-alloy (right hand) are presented in Figure 2. In contrast with what was seen just above for the {0.25C}-containing alloys, the best reproducibility was obtained for the Hf-free alloy (Co-25Cr-0.50C) while the curves corresponding to the 1200°C stage temperature show an oxidation start at higher temperature than the ones for the two other stage temperatures.

Temperatures of oxidation start

On the previous graphs presented in Figure 2 and Figure 3, one can specify for all the three curves plotted together in each of them, the temperatures at which the mass gain becomes significant enough to be detectable by the micro-balance of the Setaram TG92 thermogravimetric tester apparatus. The results can be

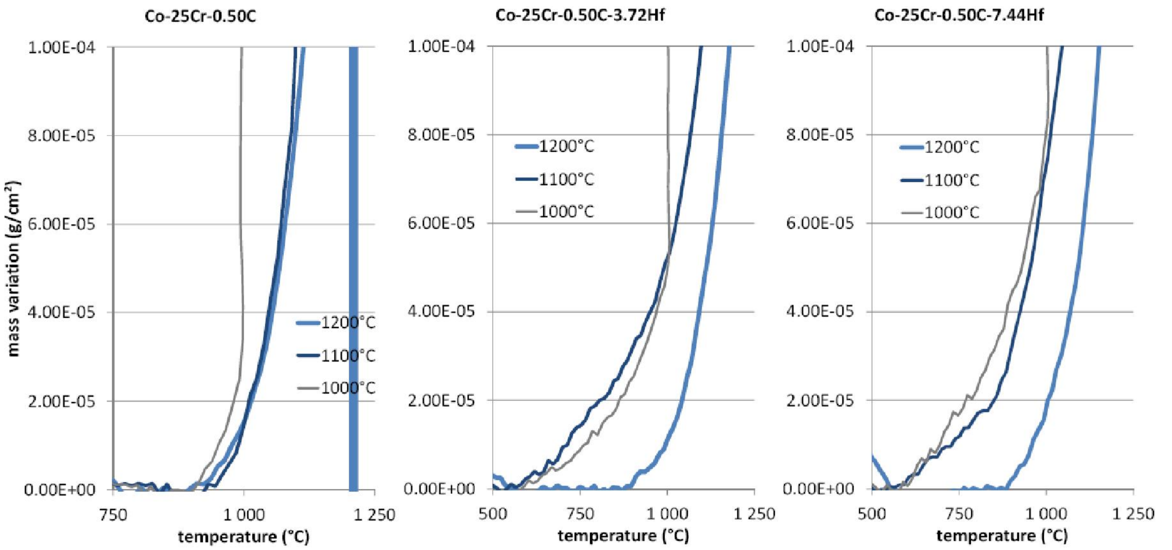


Figure 3 : Mass gain curves during heating plotted versus temperature for determination of the temperatures of oxidation start (criterion: detection of mass gain with the used thermo-balance) and for the total mass gain during the whole heating; here: the three 0.50wt.%C-containing alloys

presented in a summarized manner by drawing the histogram which is presented in Figure 4.

One can see first that cumulating the results obtained for a same alloy is rather informative about their reproducibility and then their representativeness. As qualitatively seen above for the heating parts of curves themselves the temperature of oxidation start (as defined above) is not always reproducible. Here we can think that the values are close to one another for the {0.25C-3.72Hf}-containing alloy and the {0.50C}-containing one but not really for the three others. This lack of reproducibility does not allow to conclude about the effect, on this parameter, of the carbon content and on the presence of hafnium and its amount.

Total mass gain during heating

The correction of the mass gains from air buoyancy variation also allows determining the real mass gain achieved during the whole heating. The results are presented in Figure 5 with two magnifications. The first graph (top) allows seeing globally the results for the five alloys and the three temperatures while the second one (bellow) allows distinguishing the smaller differences between the heating up to 1000°C and the one up to 1100°C, for each alloy.

First one can say that it clearly appears that: the higher the temperature the higher the mass gain (even if the 1200°C results[9] are added). Second, in contrast with what is written above about the oxidation start temperature, the total mass gain achieved during the whole heating up to 1000°C or 1100°C clearly depends on

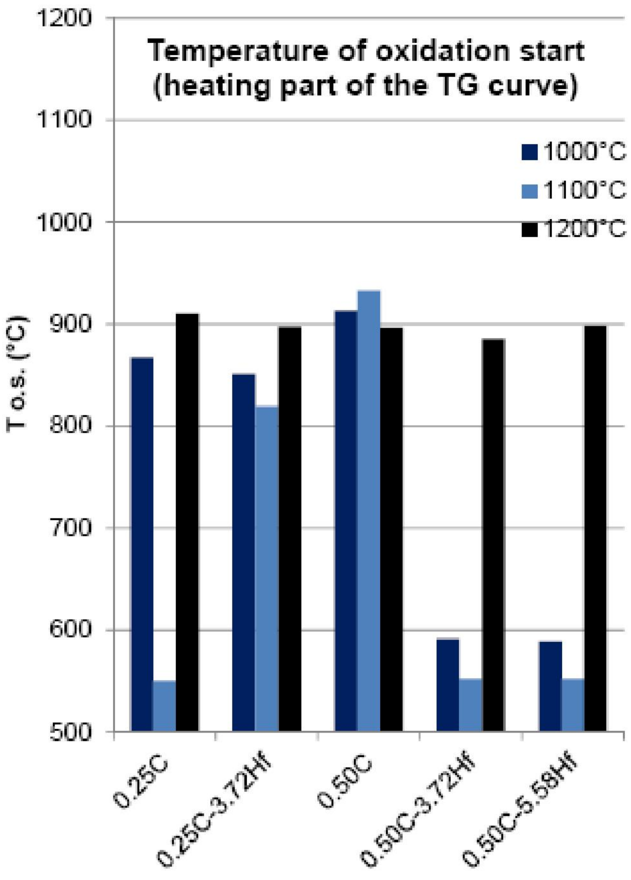


Figure 4 : Histogram presenting the values of oxidation start temperature for the five alloys when heated up to 1000 and 1100°C (this study), and also 1200°C (previous study[9])

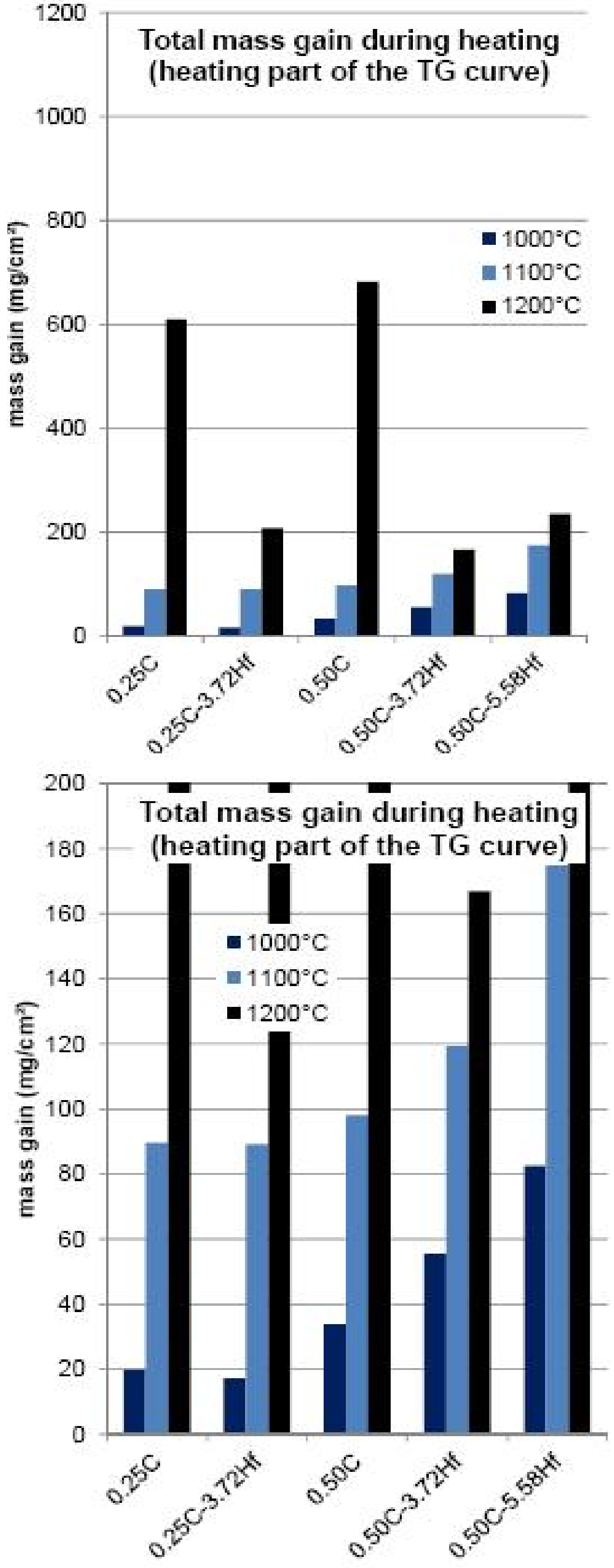


Figure 5 : Histogram presenting the values of total mass gain at the end of heating, for the five alloys when heated up to 1000 and 1100°C (this study), and also 1200°C (previous study[9]): full scale (top) and zoomed (bottom)

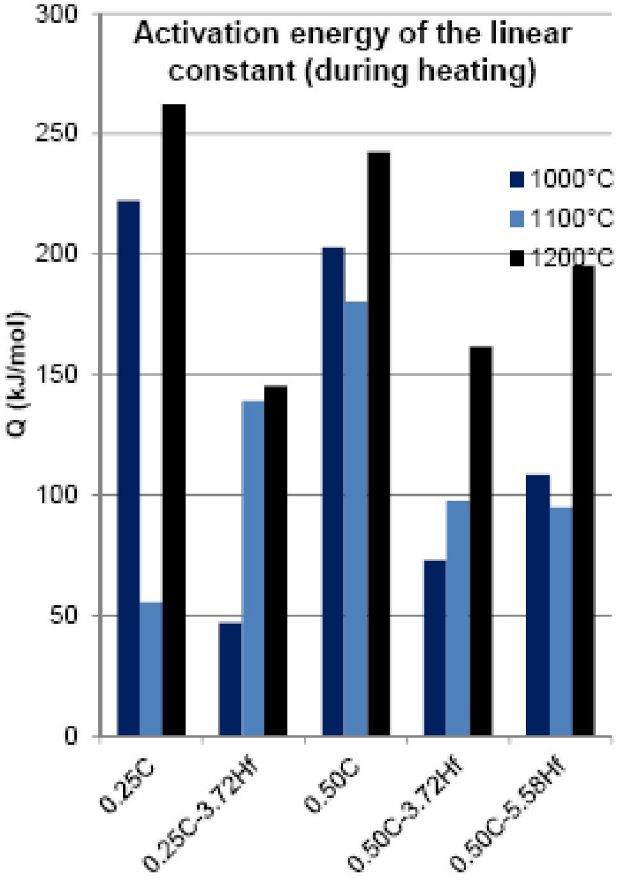
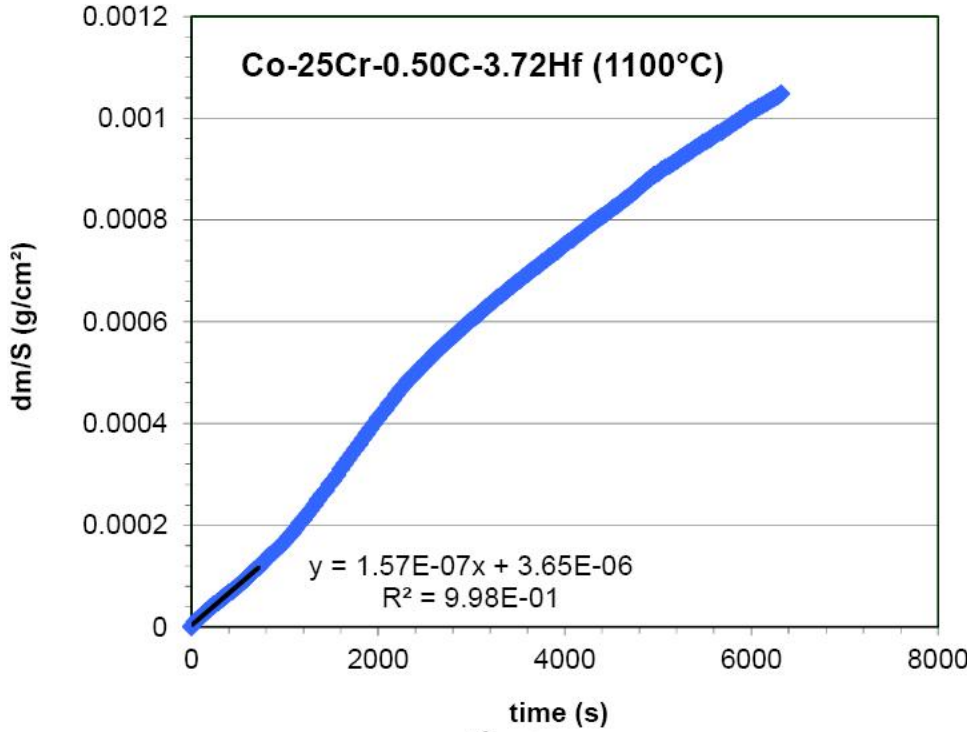


Figure 6 : Example of Arrhenius plot of the instantaneous liner constant during heating (top) and histogram presenting the values of the corresponding activation energies obtained for the five alloys when heated up to 1000 and 1100°C (this study), and also 1200°C (previous study[9])

the carbon content and on the hafnium content. Indeed, the mass gains during heating become higher when the carbon content in alloy increases from 0.25C to 0.50C for a given hafnium content, and, in the exclusive case of the {0.50wt.%C}-containing alloys, the addition of hafnium induces a heating mass gain higher than for the Hf-free alloy and, in addition, the increase in hafnium content (from the Co-25Cr-0.50C-3.72Hf alloy to the Co-25Cr-0.50C-7.44Hf one) leads to a new increase in heating mass gain. In contrast the addition of hafnium to the Co-25Cr-0.25C do not have any significant effect) whatever the temperature. When the 1200°C results[9] are added this becomes not so clear: at this temperature the addition of hafnium to the two Hf-free alloys inversely leads to the opposite results: the mass gaian achieved during heating significantly decreases.

Instantaneous linear constant versus temperature



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

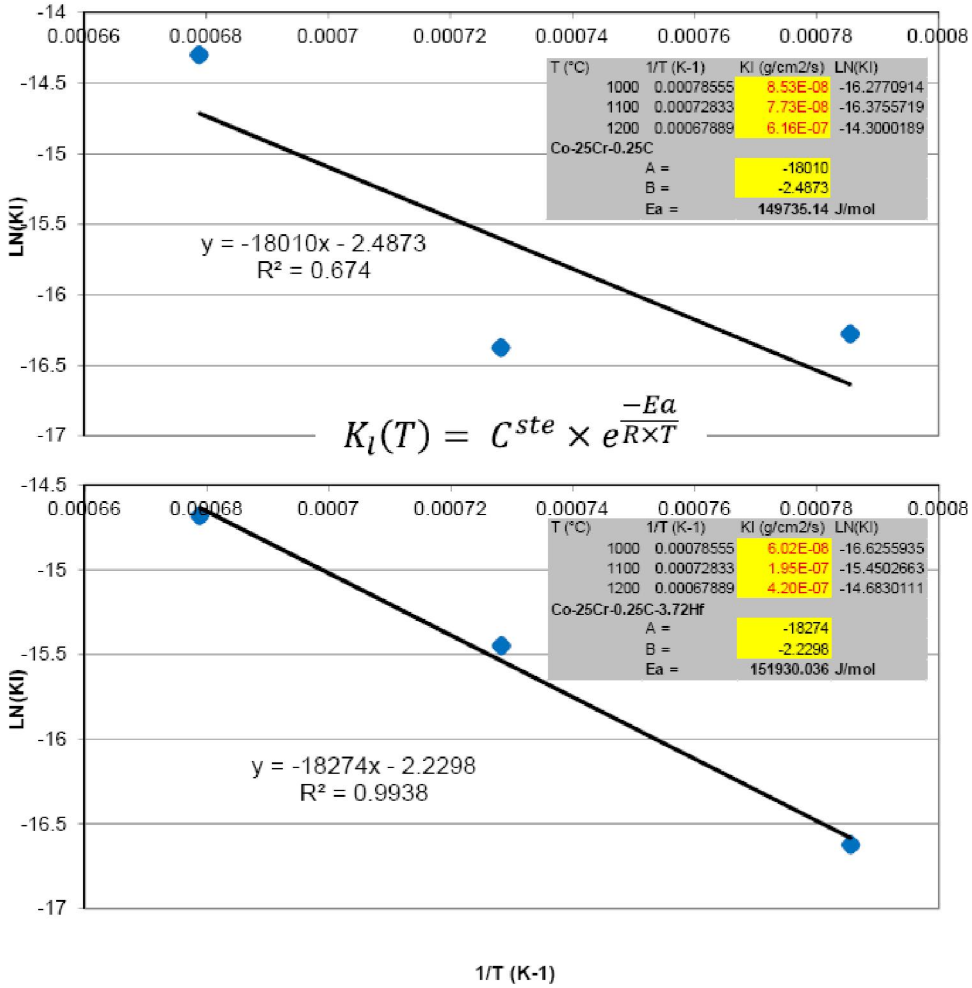
Figure 7 : Determination of the linear constant characterizing the linear transient oxidation at the beginning of the isothermal stage

After the start of oxidation as detected by the thermo-balance, it is possible to determine during the heating the instantaneous mass gain rate from the mass gains corrected from air buoyancy variation. Estimations of this rate for each successive temperature of mass gain measurement, derived number of the mass gain by time at this each recording temperature during heating, was simply done by dividing the mass gain difference by the time step. Because of the wide variation of this instantaneous linear constant (noted K_l(T)) when temperature increases from the oxidation start temperature up to the isothermal stage temperature, it is more convenient to present the results in an Arrhenius scheme. In this representation we obtained clouds of points more or less aligned. The slopes of the regression straight lines were determined, what led to the values of activation energies (after multiplication by the opposite value of the state law of the perfect gases) which are presented in Figure 6. The results are rather scattered, results for 1200°C[9] added or not. However it globally seems that adding hafnium tends to decrease 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 7 (case of the Co-25Cr-0.50C-3.72Hf 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: Co-25Cr-0.25C, bottom: Co-25Cr-0.25C-3.72Hf) and in Figure 8 for the three {0.50C}-containing alloys (top: Co-25Cr-0.50C, middle: Co-25Cr-0.50C-3.72Hf, bottom: Co-



T (°C)	1/T (K-1)	Kl (g/cm2/s)	LN(Kl)
1000	0.00078555	8.53E-08	-16.2770914
1100	0.00072833	7.73E-08	-16.3755719
1200	0.00067889	6.16E-07	-14.3000189
Co-25Cr-0.25C			
	A =	-18010	
	B =	-2.4873	
	Ea =	149735.14	J/mol

$$K_l(T) = C^{ste} \times e^{\frac{-Ea}{R\times T}}$$

T (°C)	1/T (K-1)	Kl (g/cm2/s)	LN(Kl)
1000	0.00078555	6.02E-08	-16.6255935
1100	0.00072833	1.95E-07	-15.4502663
1200	0.00067889	4.20E-07	-14.6830111
Co-25Cr-0.25C-3.72Hf			
	A =	-18274	
	B =	-2.2298	
	Ea =	151930.036	J/mol

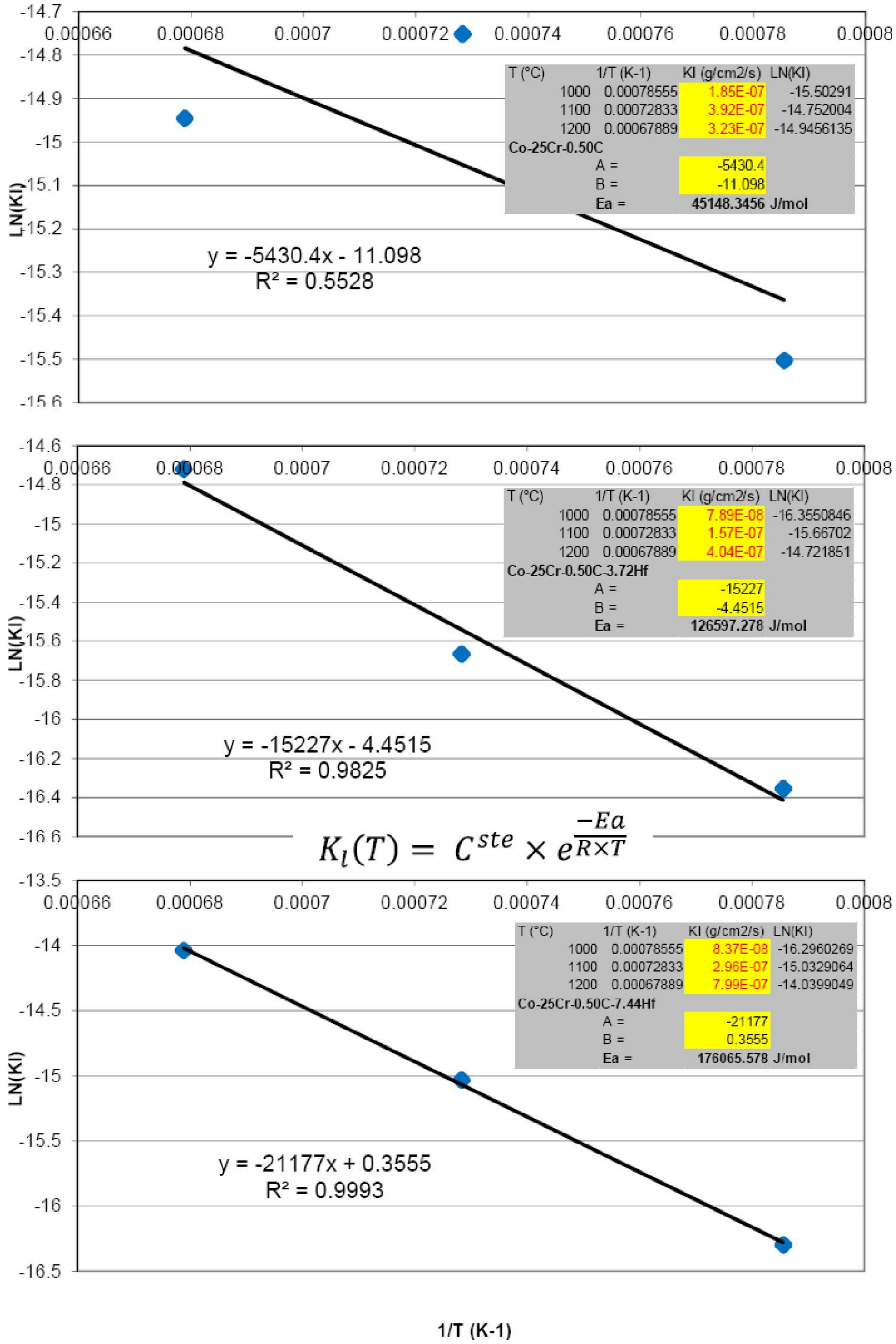
Figure 8 : Arrhenius plot and values of the K_l linear constants; value of the corresponding activation energy (for the two {0.25wt.%C}-containing alloys)

25Cr-0.50C-7.44Hf). One can see first that the three points are much better aligned for the Hf-containing alloys than for the ternary ones. For the later ones it is not reasonable to try interpreting the results which are not sure. For the three Hf-containing alloys, for which the points were well aligned, the obtained activation energies are a little scattered, with no evident evolution versus the carbon content or the hafnium content.

General commentaries

The thermogravimetry runs performed until reaching either 1000°C or 1100°C did not show a sufficient reproducibility for their common parts (i.e. from ambient temperature to 1000°C). Only two of the five alloys led to good reproducibility but this was not sufficient to evidence a possible role of the carbon content and of the hafnium content on the temperature of oxidation start. It was seen for the heating up to 1200°C that the oxidation start temperature was seemingly the same for the five alloys (close to 900°C in all cases), thus without influence of the contents in C or Hf. By performing the thermogravimetry tests with heating up to 1000°C or 1100°C for the same alloys the result evocated just above has become unclear. The values obtained for the total mass gain during heating up to 1000°C and 1100°C show effects of the C and Hf contents which are clear but different from what was seen earlier for heating up to 1200°C[9]: here it increases with the carbon content and with the hafnium content while it decreased when hafnium was added in the case of 1200°C.

Concerning the activation energies for the instantaneous linear oxidation constant at each heating step, the results were rather scattered for a same alloy by considering the heating parts of its three mass gain curves, which did not allow analyzing these results by



T (°C)	1/T (K-1)	KI (g/cm2/s)	LN(KI)
1000	0.00078555	1.85E-07	-15.50291
1100	0.00072833	3.92E-07	-14.752004
1200	0.00067889	3.23E-07	-14.9456135
Co-25Cr-0.50C			
	A =	-5430.4	
	B =	-11.098	
	Ea =	45148.3456	J/mol

T (°C)	1/T (K-1)	KI (g/cm2/s)	LN(KI)
1000	0.00078555	7.89E-08	-16.3550846
1100	0.00072833	1.57E-07	-15.66702
1200	0.00067889	4.04E-07	-14.721851
Co-25Cr-0.50C-3.72Hf			
	A =	-15227	
	B =	-4.4515	
	Ea =	126597.278	J/mol

$$K_l(T) = C^{ste} \times e^{\frac{-Ea}{R \times T}}$$

T (°C)	1/T (K-1)	KI (g/cm2/s)	LN(KI)
1000	0.00078555	8.37E-08	-16.2960269
1100	0.00072833	2.96E-07	-15.0329064
1200	0.00067889	7.99E-07	-14.0399049
Co-25Cr-0.50C-7.44Hf			
	A =	-21177	
	B =	0.3555	
	Ea =	176065.578	J/mol

Figure 9 : Arrhenius plot and values of the K_l linear constants; value of the corresponding activation energy (for the three {0.50wt.%C}-containing alloys)

regards to the chemical composition. However the presence of hafnium seemed leading to linear constants of transient oxidation at the reaching of the isothermal stage which obeyed an Arrhenius law. The corresponding activation energies were of similar levels but these ones were not really interpretable by considering the chemical composition.

CONCLUSIONS

These new oxidation tests performed up to 1000°C and 1100°C with the same Hf-free and Hf-containing

Cr-rich Co-based alloys brought new information about the characteristics of high temperature oxidation of these alloys during heating. Unfortunately no clear dependence of the oxidation characteristics were upon the chemical composition was revealed, and the possible influence of hafnium when present in high content was not really evidenced. We will continue this experimental exploration of the effects of high hafnium contents in cobalt-based alloys with the study of the isothermal oxidation and of the scale behavior during cooling in a next work[12].

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