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Effect of a high hafnium content on the high temperature oxidation of chromium-rich cast alloys. Part 1: Oxidation at heating of fe-based alloys

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ABSTRACT

Hafnium is recognized to enhance the resistance of alloys against high temperature oxidation. The effect of this element, generally added in small quantities (typically 1wt.% and less), is not known when it is present with rather high contents. In this work, cast chromium-rich iron-based alloys containing four times the usual content were tested in oxidation at 1000 and 1100°C, to complete existing works earlier realized at 1200°C. The thermogravimetric tests were done in dry synthetic air for 46 hours and the obtained mass gain files exploited in their heating part. After correction from air buoyancy variation, the curves of mass gain versus temperature were analysed. This aimed to specify the temperature of oxidation start, the total mass gain during heating, the instantaneous linear constant versus temperature as well as the linear constant representing the transient oxidation preceding the parabolic regime, and the corresponding activation energies. These characteristics describing the rate of oxidation during heating were all studied versus the contents of the alloys in carbon and in hafnium. It was attempted to extract the roles of these two elements on the different kinetic parameters of oxidation-induced mass gain during heating.

KEYWORDS

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

INTRODUCTION

Hafnium is one of the most important elements added to superalloys to improve their general behaviour in oxidation at high temperature[1]. As other reactive elements or rare earth (Y, Zr, Ce, La…) its presence in alloys notably lead to decrease in oxidation rates[2], whatever the base element. In the specific case of Fe-based alloys many results were obtained about the hafnium effect over several decades, essentially for Fe-Cr-Al alloys[3-7]. For example thirty years ago Biegun and al[3] studied the effects of hafnium (and yttrium) additions to Fe-23Cr-5Al. In 2003 Pint published a review about the improvements of alumina-forming Fe-Cr-Al alloys in high temperature oxidation thanks to the additions of reactive elements with among them: hafnium[4]. The effect of Hf and also of Zr and Ti were studied by Ishii et al[5] for Fe-20Cr-5Al-0.1La alloys and they found a decrease in high temperature oxidation rate for the alumina scales as well as for the chromia scales. The resistance of Fe-Cr-Al alloys against high temperature oxidation were also observed by Nam and

Kim[6] for isothermal conditions as well as in thermal cycling. To improve the high temperature oxidation behaviour Hf is sometimes added alone or together with other reactive elements of rare earth metals as done in some of the previously cited works. An additional example is the addition of both hafnium and lanthanum to a Fe-20Cr-5Al alloy[7].

Many of these previous works concern iron-based alloys rich not only in chromium but also in aluminium, with as result an alumina-forming behaviour of these alloys in situation of oxidation at high temperature. In addition, the weight contents in hafnium which are considered are rather low (e.g. 0.25wt.%Hf[5] or 1wt.%[6]). There is obviously a lack about the effect of hafnium on high temperature oxidation behaviour of iron-based chromia-forming alloys with Hf contents significantly higher.

It is the purpose of this work to study the effect of higher quantities in hafnium on the behaviour of chromium-rich Fe-based alloys in oxidation at high temperature. In this first paper the oxidation during heating up to two high temperatures – 1000 and 1100°C – will be characterized by thermogravimetry, for three Hf-containing alloys as well as for Hf-free alloys with the same base chemical compositions.

EXPERIMENTAL DETAILS

The alloys of the study

The iron-based alloys of the study were wished with rather high chromium content (25wt.%Cr for all of them) to allow a chromia-forming behaviour (or at least a $(Cr,Fe)_2O_3$-forming one) and two levels of carbon contents (0.25 and 0.50wt.%). The considered hafnium contents were significantly higher than the most common Hf contents: the contents considered here are 3.7 and 5.6wt.%Hf, as is to say at least four times the most common Hf contents usually added to alloys. Such alloys were previously elaborated by foundry from pure elements in order to discover and characterize the as-cast microstructures which may be obtained for Fe-25Cr alloys containing simultaneously carbon and high Hf quantities[8]. Some aspect of their oxidation behaviour were thereafter studied at 1200°C[9,10], which led to results which will be, for some of them, added to the ones of the present work to extend the analysis over the [1000, 1200°C] temperature range. Thus, there are five alloys considered for the present study (name, followed by the chemical composition obtained by Energy Dispersive Spectrometry):

- "Fe-25Cr-0.25C-3.72Hf": 25.71wt.% Cr and 3.87wt.%Hf (Co: bal., C: not measured)
- "Fe-25Cr-0.50C-3.72Hf": 25.59wt.% Cr and 3.46wt.%Hf (Co: bal., C: not measured)
- "Fe-25Cr-0.50C-5.58Hf": 27.23wt.% Cr and 4.85wt.%Hf (Co: bal., C: not measured)

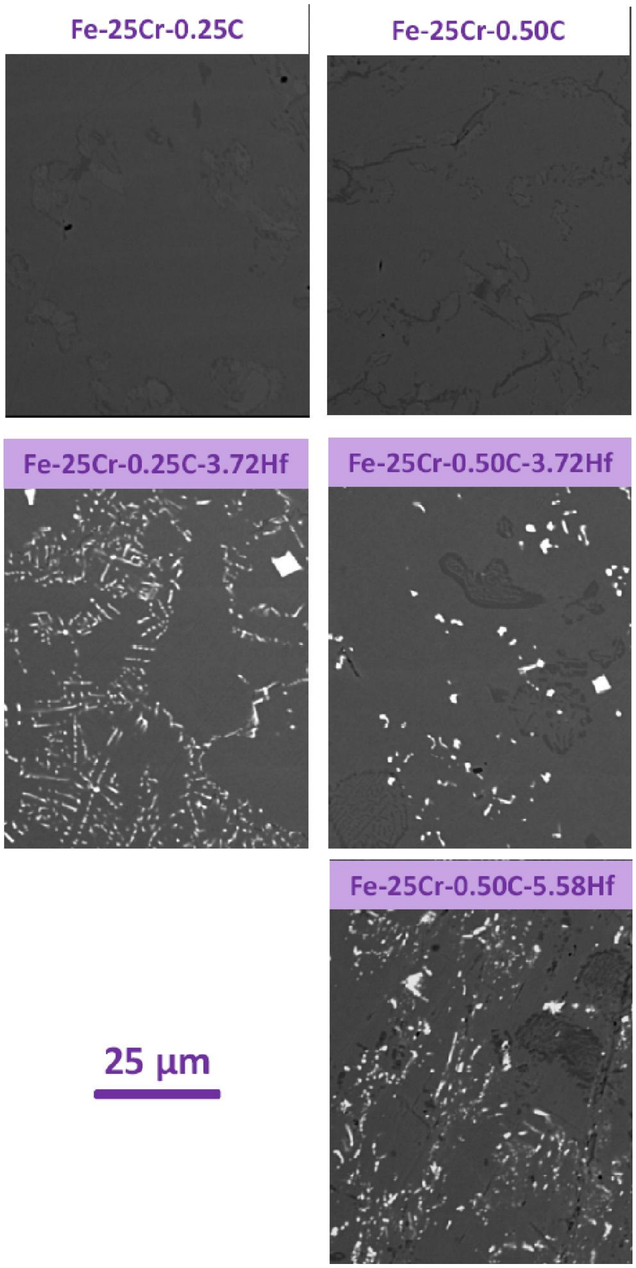


Figure 1 : Micrographs illustrating the as-cast microstructures of the five studied alloys (Scanning Electron Microscope JEOL JSM-6010LA, Back Scattered Electrons mode)

- “Fe-25Cr-0.25C”: 25.47wt.% Cr (Co: bal., C: not measured)
- “Fe-25Cr-0.50C”: 24.52wt.% Cr (Co: bal., C: not measured)

Their as-cast microstructures, reminded by the micrographs presented in Figure 1, were previously described[8]. To summarize one can say that all alloys present a dendritic matrix composed of an iron-chromium solid solution, and carbides of two types: hafnium carbides and sometimes chromium carbides in the Hf-containing alloys, only chromium carbides in the Hf-free alloys).

Preparation of the samples for the thermogravimetry tests

The five ingots were cut in the ingot’s centre to obtain samples with an almost parallelepiped geometry. They were ground with 240-grade SiC papers for smoothing the edges and the corners. Thereafter the samples were wholly polished with 1200-grade SiC paper. The thermogravimetry runs were performed with a thermobalance (Setaram TG92), in a continuous flow

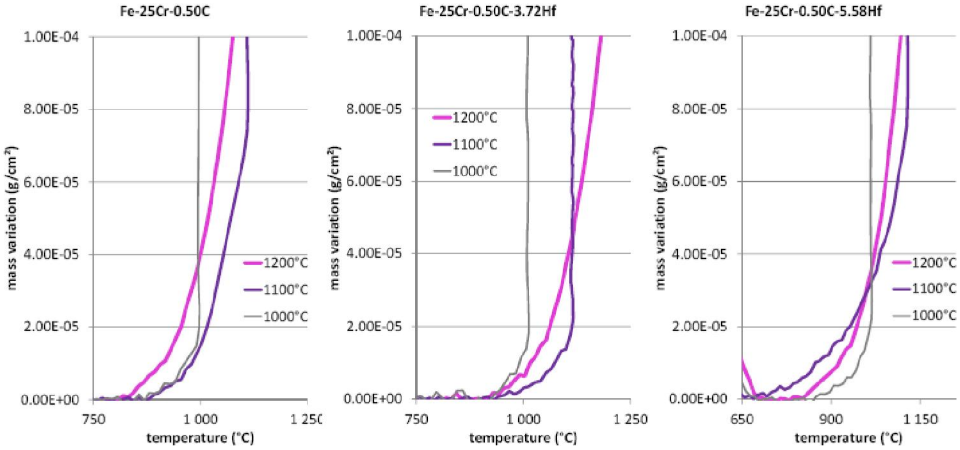


Figure 2 : Mass gain curves during heating plotted versus temperature for determination of the temperatures of oxidation start (criterion: detection of mass gain with the used thermo-balance) and for the total mass gain during the whole heating; here: the two 0.25wt.%C-containing alloys

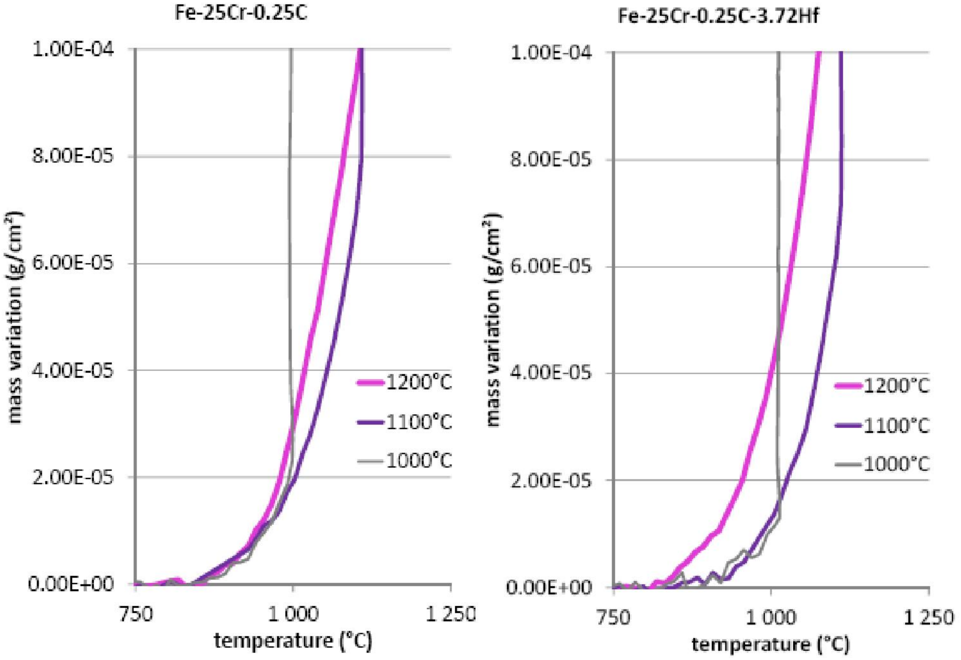


Figure 3 : Mass gain curves during heating plotted versus temperature for determination of the temperatures of oxidation start (criterion: detection of mass gain with the used thermo-balance) and for the total mass gain during the whole heating; here: the three 0.50wt.%C-containing alloys

of dry artificial air (80%N_2-20%O_2).

The thermal cycle was composed of the following successive steps:

- heating at 20°C min^{-1},
- isothermal (1000 or 1100°C)-stage during 46 hours
- cooling at -5°C min^{-1}

The exploitations of the heating parts of the mass gain files were done according to the procedures described in an earlier work[11]. In a first time, the mass gains were plotted versus temperature (and not time as usually done) to obtain an equation which allows correcting the mass gains from the variations of air buoyancy. The mass gains were then plotted again and the following data were deduced from the obtained new curves:

- temperature of oxidation starts to be significant enough to allow a detectable mass gain
- evolution of the linear constant between the oxidation start temperature and the stage temperature;
- analysis in the Arrhenius scheme and determination of the corresponding activation energy
- total mass gain achieved during heating.

Additionally, the mass gain rate existing just after that temperature reached the isothermal stage temperature was considered: the slope of the tangent straight line (mass gain conventionally represented again: 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).

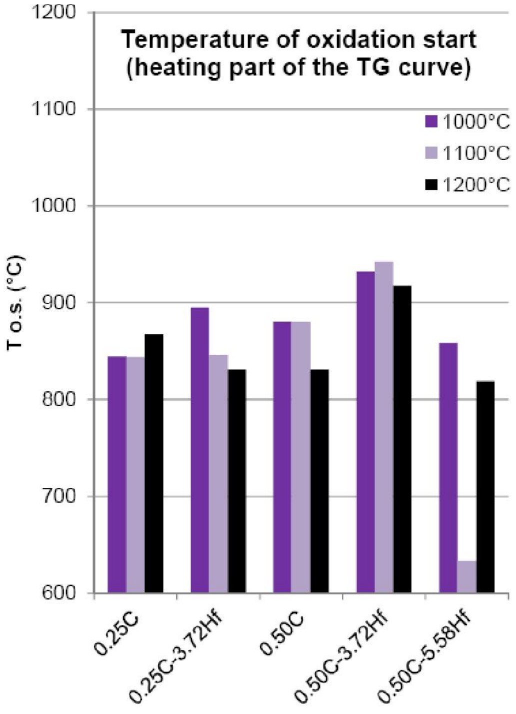


Figure 4 : Histogram presenting the values of oxidation start temperature for the five alloys when heated up to 1000 and 1100°C (this study), and also 1200°C (previous study[9])

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]. One can see that the oxidation during heating of the Hf-free alloy presents a good reproducibility for the common part of the three curves (T<1000°C). In contrast it is not the case for the Hf-containing alloy since the sample destined to the 1200°C oxidation test seems having oxidized much faster than the ones destined to isothermal oxidation at 1000 and 1100°C, although the test conditions were of course the same for the three samples during heating bellow 1000°C.

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 3. There is, this time for the three alloys Hf-free or Hf-containing, a lack of reproducibility.

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 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

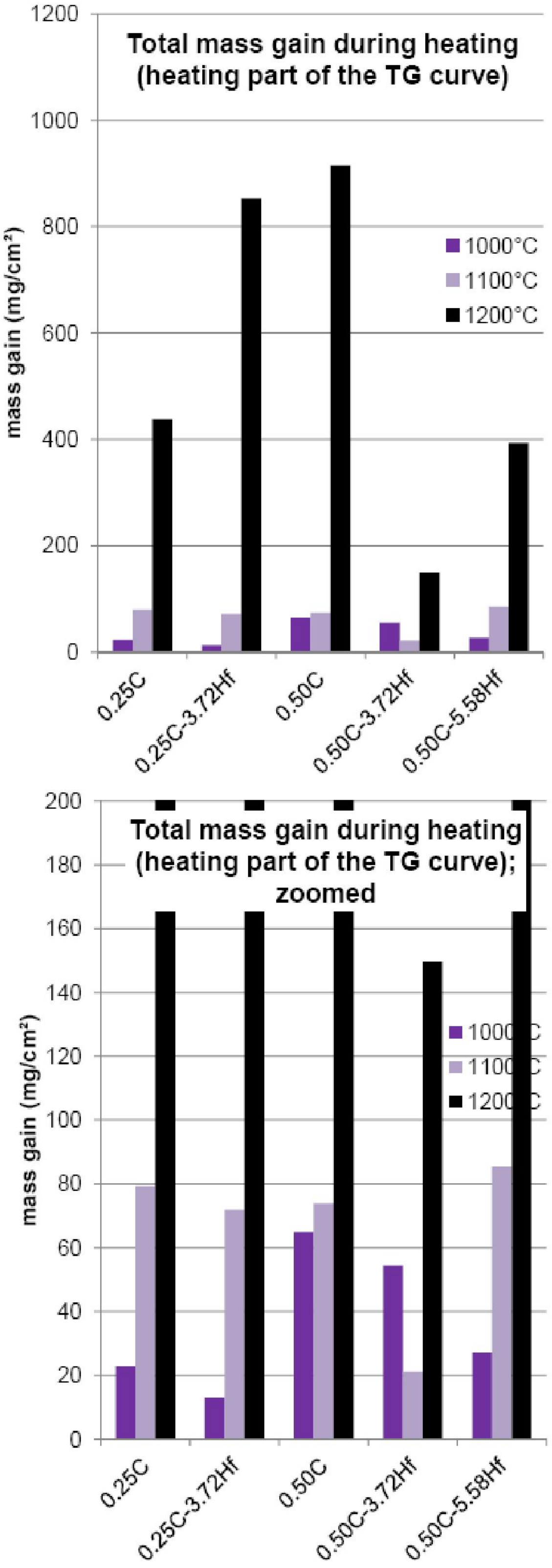


Figure 5 : Histogram presenting the values of total mass gain at the end of heating, for the five alloys when heated up to 1000 and 1100°C (this study), and also 1200°C (previous study[9]): full scale (top) and zoomed (bottom)

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}-alloy and the {0.50C-3.72Hf}-alloy but not really for the three others. The results are particularly scattered for the {0.50C-5.58Hf}-alloy for which oxidation start was detected at an especially low temperature for one of the three curves (the one for which the future temperature of isothermal oxidation is 1100°C).

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) allow 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.

One can see first that the higher the temperature the higher the mass gain. However there is an exception in the case of the {0.50C-3.72Hf}-alloy for which the values obtained for 1100°C is curiously lower than for 1000°C.

One can note in Figure 5 (top) that the mass ain achieved during heating is particularly high for 1200°C: this can be explained by the same time spent at temperatures globally very high (between 1100 and 1200°C, oxidation much faster) as the time spent at lower temperatures before (oxidation much slower). In contrast, for 1200°C, no systematic effect of the carbon content or of the hafnium one was revealed: the mass gain after heating until reaching 1200°C seems increasing with the carbon content when Hf is absent in the alloy while it is the contrary when Hf is present. Similarly, this mass gain seems increasing with the presence of hafnium when the carbon content is 0.25wt.%C while it decreases when the latter one is 0.50wt.%.

The results for 1100 and 1000°C are better represented in Figure 5 (bottom). For these two lowest temperatures, it seems that – despite rare exceptions – the

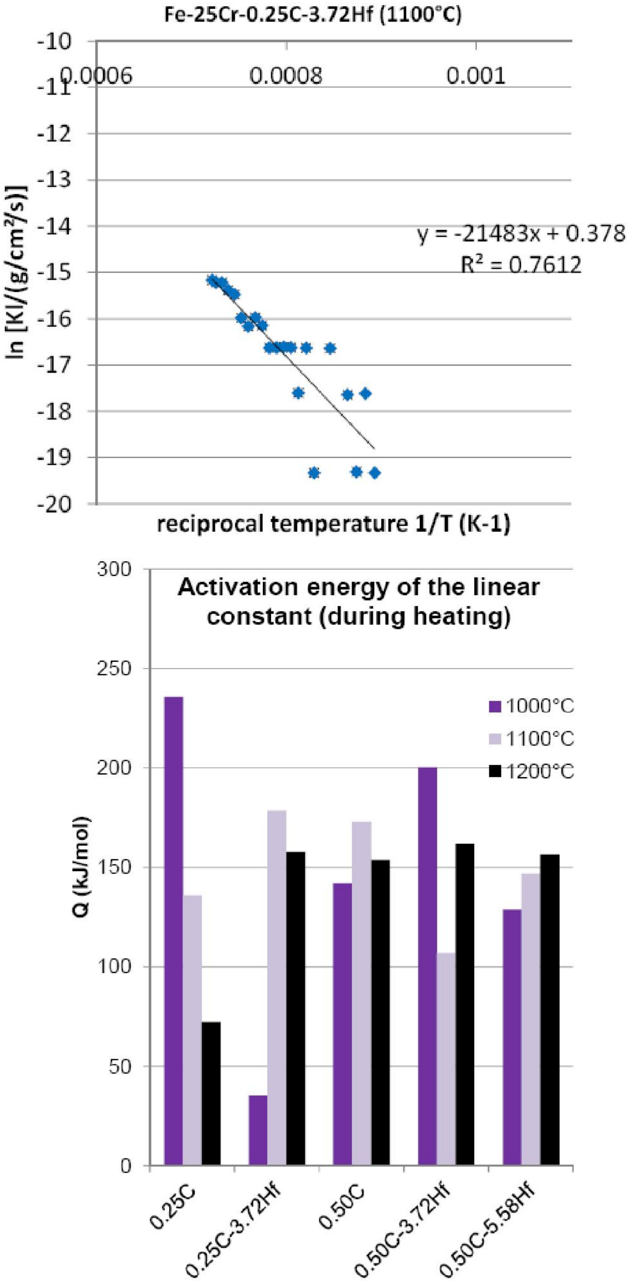
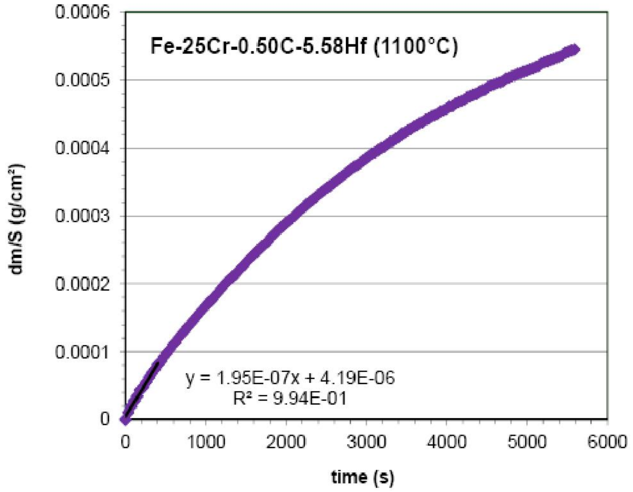


Figure 6 : Example of Arrhenius plot of the instantaneous liner constant during heating (top) and histogram presenting the values of the corresponding activation energies obtained for the five alloys when heated up to 1000 and 1100°C (this study), and also 1200°C (previous study[9])

Instantaneous linear constant versus temperature

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. An example of such graph (Fe-25Cr-0.25C-3.72Hf heated up to 1100°C) is presented in Figure 6 (top). One can see that the Kl(T) globally increases with temperature but also that it seems obeying an Arrhenius law more for the highest temperatures (left side of the graph) than for the lowest ones (right side). This was generally observed, especially for the heating up to 1100 or 1200°C. The activation energies deriving from these Arrhenius plot were the most often determined on the most linear parts of Arrhenius graphs (i.e. on the left, high temperatures side) except when the good linearity of $\ln\{K_l(T)\}$versus the reciprocal temperature (1/T in K^{-1}) was observed for all the graph.

The results are presented in the bottom part of Figure 6. The results appear rather scattered when the three stage temperatures are considered. By considering only the two highest stage temperatures, the heating to which mass gain achieved during heating tends to increase with the carbon content (in absence of hafnium as well as in its presence) and to decrease when hafnium is present.



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

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

necessarily includes temperatures high enough to get a good curve linearity in Arrhenius plot, it seems that the activation energy increases with the presence of hafnium for the {0.25C}-containing alloys but remains at a maximal level for the {0.50C}-containing alloys, independently on the presence of hafnium.

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

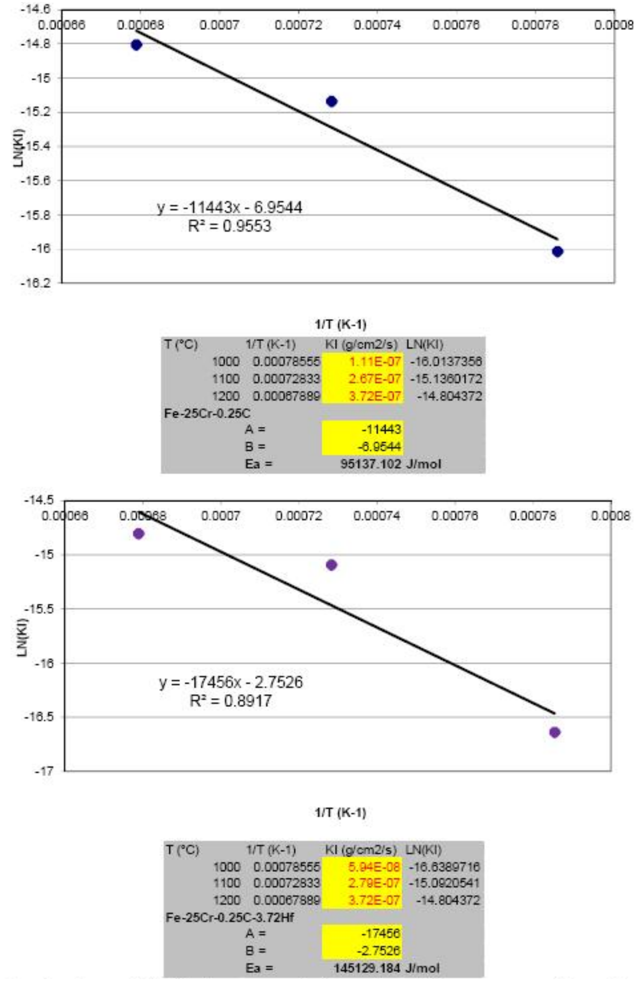
The final kinetic characteristic of the mass gain during heating is the rate at which the mass gain continues its increase in the first times of the isothermal stage. Without correction from air buoyancy variation (temperature has now become constant), the mass gain files present a more or less long 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 Fe-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 8 for the two {0.25C}-containing alloys (top: Fe-25Cr-0.25C, bottom: Fe-25Cr-0.25C-3.72Hf) and in Figure 9 for the three {0.50C}-containing alloys (top: Fe-25Cr-0.50C, middle: Fe-25Cr-0.50C-3.72Hf, bottom: Fe-25Cr-0.50C-5.58Hf). One can see first that the three points are more (e.g. Fe-25Cr-0.50C-5.58Hf) or less (e.g. Fe-25Cr-0.50C-3.72Hf: very bad alignment due to K_l higher for 1000 than for 1100°C!) aligned.

The activation energy seems to be independent on the carbon content by considering their values obtained for the two Hf-free alloys (95kJ/mol). It is also not dependent on the presence of Hf and on its content when the carbon content is 0.50wt.%C (it varies between 92 and 100kJ/mol) while it seems existing a dependence of the presence of Hf when the carbon content is 0.50wt.%C (145 kJ/mol for the Fe-25Cr-0.25C-3.72Hf alloy against the 95kJ/mol of the corresponding Hf-free alloy).

General commentaries

Thus, there was often a lack of reproducibility of the whole heating part of the mass gain curves. This was evidenced by comparing the mass gain plotted versus temperature from the measurement files obtained in the present work (1000 and 1100°C) and also by involving previous work done at 1200°C. The three curves plotted together per alloy were effectively not always superposed for their common temperature ranges (Figure 2 and Figure 3) and this logically led to values of oxidation start temperatures a little (and "very" for one of the five alloys) dispersed. Fortunately this did not hinder the absence of dependence of this temperature on the carbon and hafnium presence and/or content. An exception: the Fe-25Cr-0.50C-3.72Hf which seemed starting to oxidize at a slightly higher temperature than for the other alloys.

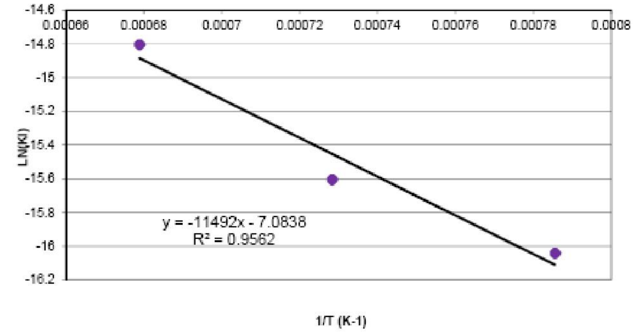


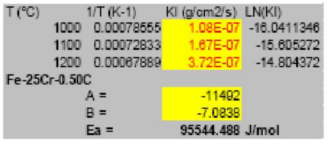
T (°C)	1/T (K-1)	KI (g/cm2/s)	LN(KI)
1000	0.00078555	1.11E-07	-16.0137356
1100	0.00072833	2.67E-07	-15.1360172
1200	0.00067889	3.72E-07	-14.804372
Fe-25Cr-0.25C			
	A =	-11443	
	B =	-6.9544	
	Ea =	95137.102 J/mol	

T (°C)	1/T (K-1)	KI (g/cm2/s)	LN(KI)
1000	0.00078555	5.94E-08	-16.6389716
1100	0.00072833	2.79E-07	-15.0920541
1200	0.00067889	3.72E-07	-14.804372
Fe-25Cr-0.25C-3.72Hf			
	A =	-17456	
	B =	-2.7526	
	Ea =	145129.184 J/mol	

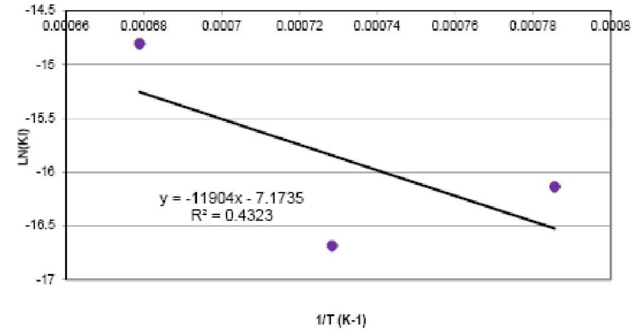
Figure 8 : Arrhenius plot and values of the K_l linear constants; value of the corresponding activation energy (for the two {0.25wt.%C}-containing alloys)

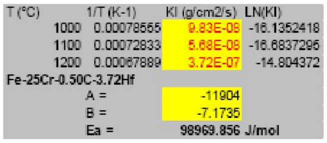
The mass gains during the whole heating were logically much higher for 1100°C than for 1000°C (with however two exceptions: Fe-25Cr-0.50C and Fe-25Cr-0.50C-3.72Hf), and much higher for 1200°C than for 1100°C. This is totally logical since the instanta-



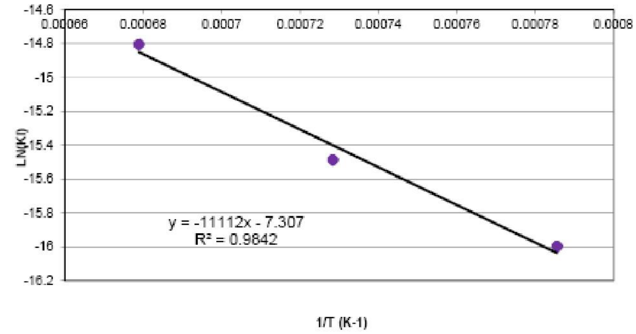


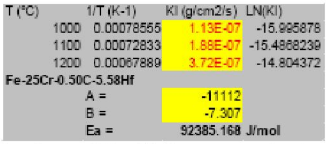
T (°C)	1/T (K-1)	Kl (g/cm2/s)	LN(Kl)
1000	0.00078555	1.08E-07	-16.0411346
1100	0.00072833	1.67E-07	-15.605272
1200	0.00067889	3.72E-07	-14.804372
Fe-25Cr-0.50C			
	A =	-11492	
	B =	-7.0838	
	Ea =	95544.488	J/mol





T (°C)	1/T (K-1)	Kl (g/cm2/s)	LN(Kl)
1000	0.00078555	9.83E-08	-16.1352418
1100	0.00072833	5.68E-08	-16.6837295
1200	0.00067889	3.72E-07	-14.804372
Fe-25Cr-0.50C-3.72Hf			
	A =	-11904	
	B =	-7.1735	
	Ea =	98969.856	J/mol





T (°C)	1/T (K-1)	Kl (g/cm2/s)	LN(Kl)
1000	0.00078555	1.13E-07	-15.995878
1100	0.00072833	1.88E-07	-15.4868239
1200	0.00067889	3.72E-07	-14.804372
Fe-25Cr-0.50C-5.58Hf			
	A =	-11112	
	B =	-7.307	
	Ea =	92385.168	J/mol

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

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)

neous oxidation rate increased more and more rapidly with temperature as illustrated in Figure 5 (top). But the influence of, on the one hand the carbon content, and on the other hand the presence of hafnium and its content, is not clear. Indeed, different variations versus the C content and the Hf content were seen for the three temperatures: this may be a consequence of a lack of reproducibility or of rather complex oxidation phenomena, or of a synergetic dependence of the contents in the two elements (with possibly also a direct influence of the microstructure). The variations of the activation energies corresponding to the instantaneous linear constant and to the transient liner constant at the beginning of the isothermal stage are also rather difficult to interpret. It seems existing some influence of the carbon and hafnium contents but the two sets of values of activation energy (instantaneous constant at a given temperature during heating and transient linear constant at this temperature when it is the isothermal stage beginning) are not really consistent. They are in good agreement for the 0.25wt.%C-containing alloys but the activation energy of the transient linear constants at isothermal stage beginning is 50kJ/mol lower than the ones determined during heating.

CONCLUSIONS

Realizing new oxidation tests on the same Hf-free and Hf-containing Cr-rich Fe-based alloys, by targeting for the isothermal stage two temperatures lower than the one already applied in a previous work (1200°C), allowed enriching the characteristics of oxidation of these alloys during heating. Unfortunately this revealed a more or less extended dispersion of the results for the studied parameters, which however allowed to learn that there is rarely clear effect of the carbon content and of the presence of hafnium (and of its content when present). The variations which were seen may reveal complex interactions between the different parameters, which need to be deeper studied for example by adding new alloys with intermediate compositions as well as by metallographically characterizing the oxidized samples. The same new mass gain files will be analyzed again, this time concerning the isothermal oxidation and the scale behavior during cooling, in a next article[12].

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