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High temperature oxidation of iron-based alloys reinforced by hafnium carbides. Part 1: Thermogravimetry results

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ABSTRACT

A third family of chromium-rich alloys containing interdendritic HfC carbides for their mechanical resistance at high temperatures, based on iron, was studied in oxidation at high temperature by thermogravimetry. One considered separately the oxidation kinetic during heating, during the isothermal stage and during cooling. Three quaternary alloys, containing 25wt.%Cr, 0.25 to 0.50wt.%C, and 3.72 to 5.58wt.%Hf, were subjected to the same thermal cycle as previously done for similar HfC-containing nickel-based and cobalt-based alloys. Here too the oxidation start temperature at heating, total mass gain during heating, isothermal mass gain, temperature of spallation start at cooling were especially examined, with comparison with ternary Fe-25C-0.25C and 0.50C alloy, to specify the possible effects of the carbon content and of the presence of hafnium and of its content. Globally the oxidation behaviour of the HfC-containing iron-based alloys was good, at the level of the corresponding nickel-based alloys. Notably, isothermal mass gain kinetic was rather slow and a significantly improved resistance against oxide spallation was observed for the alloys containing HfC carbides. These results were thereafter compared with the similar ones previously obtained for the corresponding HfC-containing cobalt-based and nickel-based alloys.

KEYWORDS

Iron-based alloys;
Hafnium carbides;
Transient oxidation;
High temperature oxidation;
Oxide spallation.

INTRODUCTION

With a melting point as high as 1535°C[1] iron is more refractory than nickel and even cobalt. If the latter elements are usually chosen as bases for not too expensive metallic alloys for high temperature applications (nickel-based and cobalt-based superalloys) since now fifty or sixty tens of years[2,3], iron is also considered but the most often alloyed with nickel, which leads to {iron, nickel}-based superalloys, instead alloys based only on iron. With the addition of several tens percents of chromium for hot corrosion resistance purpose[4] iron – which is subjected to an allotropic $\alpha \leftrightarrow \gamma$ solid state transformation near 910°C – is stabilized in the ferritic α form. This not compact Bravais's crystalline network[5] is *a priori* not favourable for good mechanical properties at high temperature, by comparison with compact austenitic crystalline network. Despite their very high solidus temperatures alloys based on iron-chromium need to be seriously reinforced, for example by carbides. With addition of carbon and tantalum in equivalent atomic proportions the interdendritic precipitation of TaC carbides can be successfully obtained, this leading to very refractory alloys with high solidus temperatures (around 1400°C). This potentially leads also to good mechanical resistance at high temperature, but only on short times since severe degradation of the TaC carbides was observed after only 50 hours of exposure at 1200°C[6]. The sustainability of such alloys needs carbides much more thermally stable to be resistant enough against such high temperature deterioration. By reproducing for a Fe(Cr) base what was earlier done in a Co(Cr) one[7], HfC carbides were recently successfully obtained in {25wt.%Cr}-containing iron-based alloys[8]. But interrogations remain about the real behaviour of the obtained HfC carbides at high temperature in terms of {nature, volume fraction, morphology} variations as well as of high temperature oxidation.

To answer these questions thermogravimetry tests were here performed at high temperature to investigate, for the alloys previously obtained and characterized in their as-cast condition[8], the possible transformations of the bulk HfC carbides, and of course to value the oxidation kinetics what is done in this first part with an eye of isothermal oxidation rate but also on what happens during heating and during cooling.

EXPERIMENTAL DETAILS

The alloys of the study

The three HfC-strengthened iron-based alloys were previously[8], as well as two iron-based ternary ones displaying the same chromium and carbon contents elaborated from pure elements by high frequency induction melting under inert atmosphere and rather rapidly solidified and microstructurally characterized. The names of the five alloys and their obtained chemical compositions (measured by Energy Dispersion Spectrometry) are the following:

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

Preparation of the samples for the thermogravimetry tests

The five ingots were cut in the ingot's centre to obtain almost parallelepipeds. They were grinded with 240-grade SiC papers (with smoothing of edges and corners) then wholly polished with 1200-grade ones. The thermogravimetry runs were realized using a Setaram TG92 thermobalance, with circulation of dry artificial air (80%N_2-20%O_2). The thermal cycle was composed of an heating at 20°C min^{-1}, an isothermal 1200°C-stage during 46 hours and a cooling at -5°C min^{-1}. The exploitations of the mass gain files for the heating part and for the cooling part were done according to the procedures described in earlier works [9,10].

RESULTS AND DISCUSSION

Initial microstructures of the alloys

One can remind that the three HfC-containing iron-based alloys effectively contain HfC carbides in their interdendritic spaces, appearing in white when the metallographic samples are observed with a Scanning Electron Microscope in Back Scattered mode (example in Figure 0). The 0.25wt.%C-containing alloy presents only HfC carbides while the two 050wt.%C-containing ones also contain chromium carbides (darker than

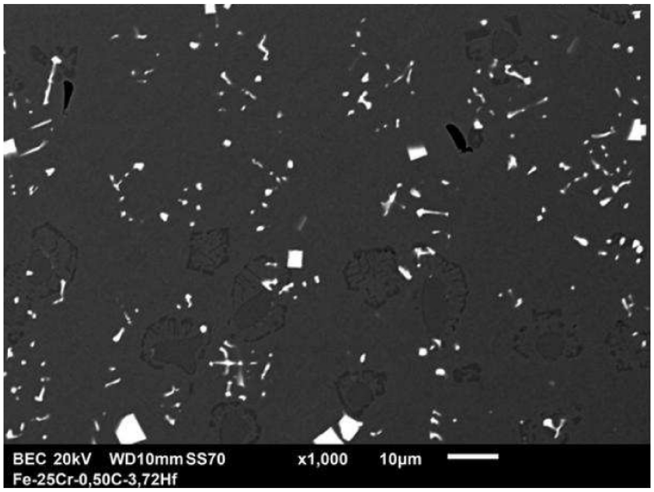

Figure 0 : Example of as-cast microstructure of a HfC-strengthened alloy (here : Fe-25Cr-0.5C-3.72Hf alloy)

matrix in the same observation conditions). The two ternary Fe-25Cr-0.25 and 0.50C alloys only contain chromium carbides.

Oxidation at heating

To better examine what happened during heating and thereafter cooling, the mass gain files were plotted versus temperature instead time (example of such curve given in Figure 1) corrected from air buoyancy variation. They were thereafter analyzed in their heating part to determine the temperature of oxidation beginning (defined as mass gain significant enough to be detected by the used thermo-balance).

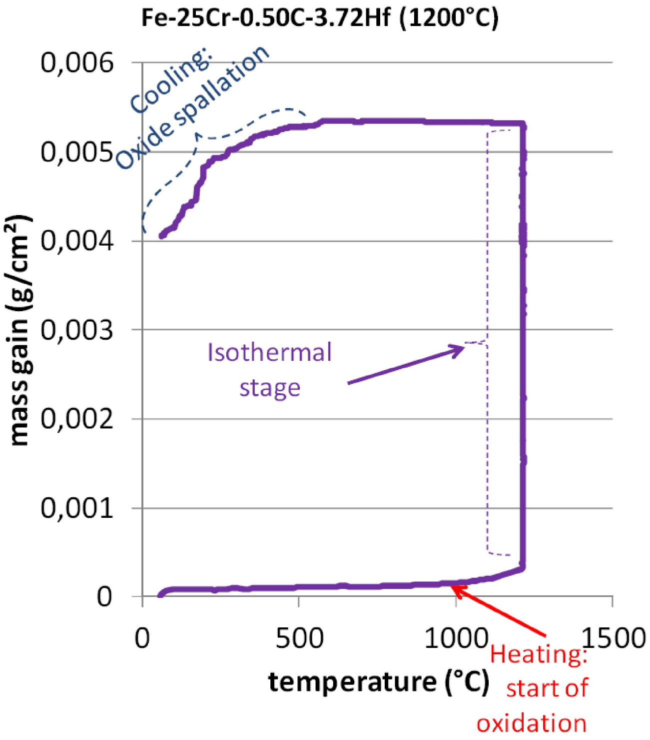

Figure 1 : Example of a mass gain curve plotted versus temperature instead versus time (evidencing the start of oxidation at the end of heating and the oxide spallation during cooling)

The obtained values of this Temperature of oxidation start (T o. s.) are graphically presented in Figure 2. By considering only the ternary alloys and the Fe-25Cr-0.25C-3.72Hf and Fe-25Cr-0.50C-5.58Hf alloys, there should be a tendency of first lower oxidation start temperatures for a higher carbon content and second for the HfC-containing alloys. This can be explained first by a better exposition to the oxidizing air of the most oxidable elements (chromium and hafnium) which belong to the interdendritic carbides than the same atoms but present in solid solution in the matrix. Indeed chromium more easily diffuses outwards along interdendritic boundaries to be externally oxidized while oxygen atoms more easily diffuse inwards by the same paths to internally oxidize carbides. Second, hafnium being particularly oxidable it can be expected that oxidation of hafnium atoms or hafnium carbides occur when temperature is not yet very high. However there was a curious result about the Fe-25Cr-0.50C-3.72Hf alloy which starts being significantly oxidized only a temperature particularly high by comparison with the other alloys.

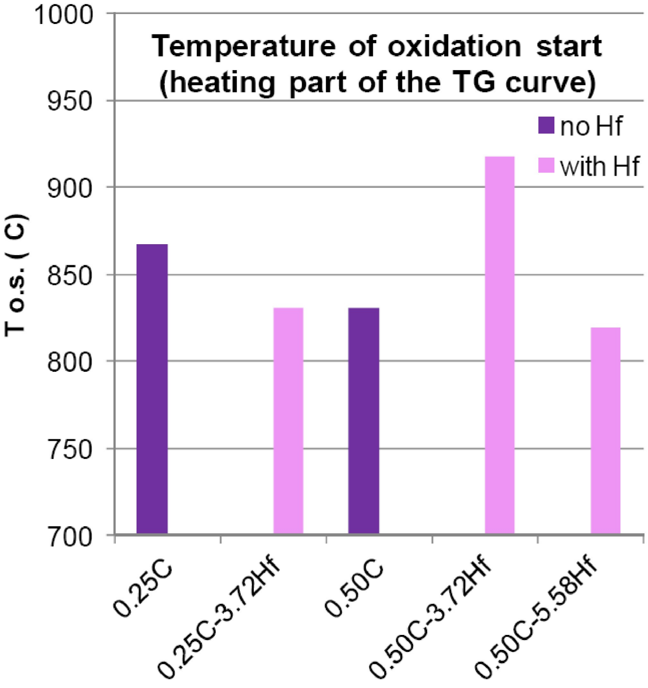

Figure 2 : Temperatures at which the mass gain due to real oxidation became detectable by the thermo-balance during the heating, for each of the five alloys (Fe-25wt.%Cr-xC-(yHf))

The total mass gain achieved by oxidation during heating is also graphically given for the five alloys, in Figure 3. Here too, if the case of the Fe-25Cr-0.50C-3.72Hf alloy is removed one can see that this mass gain measured at the beginning of the isothermal stage after corrections from the air buoyancy variations tends depending on the carbon content in presence of Hf or not. A possible reason to that can be the easier chromium supplying in presence of more carbides in the interdendritic spaces (higher availability of Cr in the high diffusion paths, higher density of matrix-carbides interfaces emerging on extreme surface). Although Hf is especially oxidable it can influence – more precisely improve – the high temperature oxidation behaviour of alloys. It can be the reason of the lower mass gains at heating observed here for a same carbon content when Hf is present. The Fe-25Cr-0.50C-3.72Hf plays alone a special role since the mass gain during heating is much lower than for all the four other alloys.

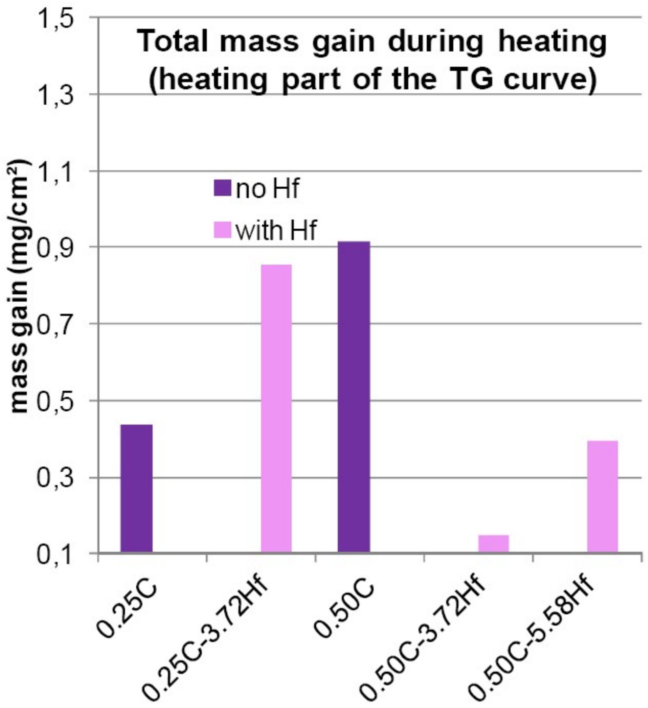

Figure 3 : The total mass gain achieved during the heating, for each of the five alloys (Fe-25wt.%Cr-xC(-yHf))

The instantaneous oxidation rate increasing with temperature during heating it can be interesting to see wether the linear transient oxidation kinetic follows or not an Arrhenius law, which may be characteristic of special mechanism of oxidation. For that the value of the instantaneous linear constant was calculated for each temperature, from the data files corrected from the air buoyancy variation again, according to $K_l(T_n) = [(\Delta m/S)_{n+1} - (\Delta m/S)_n] / (T_{n+1} - T_n)$ in which n is the step number, T_n the corresponding value and $(\Delta m/S)_n$ the corresponding mass gain per cm². $K_l(T)$ was plotted in the Arrhenius scheme for the two Hf-free iron-based alloys in Figure 4 and for two of the three Hf-containing ones in Figure 5, in the temperature range defined by the temperature of oxidation start of the alloy (as earlier defined) and the stage temperature (1200°C). All the obtained curves can be considered as straight lines (i.e. the kinetic obeys an Arrhenius law), which let thinking that the mechanisms involved in the oxidation phenomenon remain probably of same nature during the whole heating. Regression lines were then determined and their equations brought values for the activation energies (slope multiplied by the perfect gas constant R = 8.314 J mol^{-1} K^{-1}).

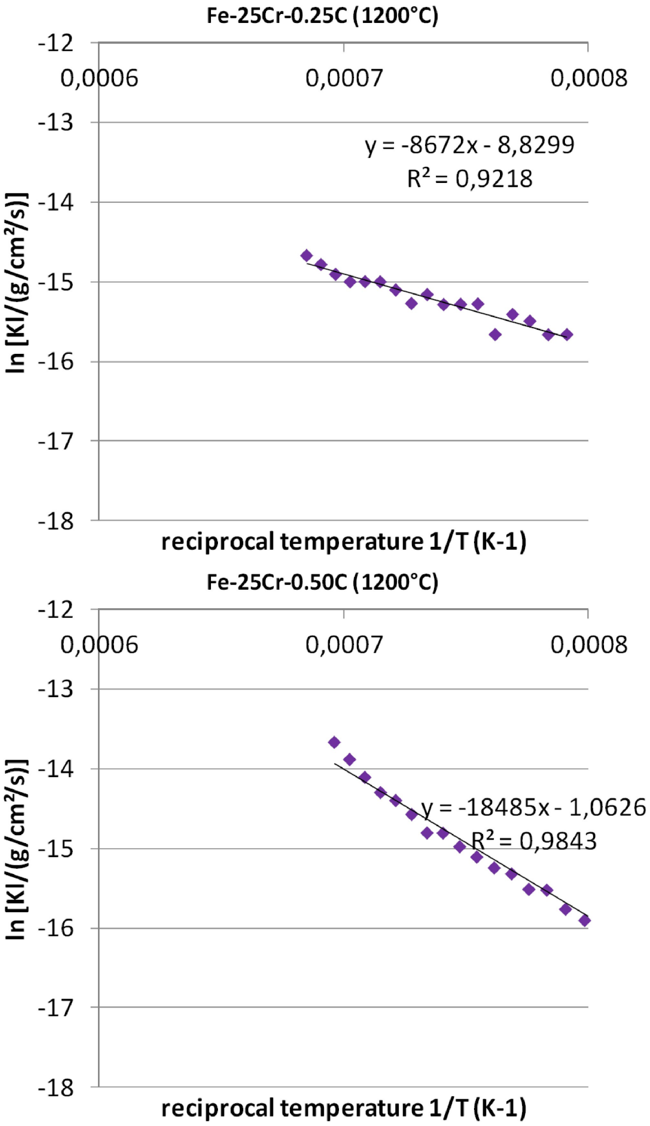

Figure 4 : Arrhenius plot of the linear constant K_l for the two Hf-free ternary alloys

The obtained values of activation energy are presented as histogram for the five alloys, in Figure 6. One can see that the activation energies are all near 150kJ mol-1, except for the Fe-25Cr-0.25C for which it is only half this value. This alloy, the one with the minimal volume fraction of carbides, seemingly behaves differently in oxidation during heating, this being possibly due to a particularly low density of carbides-occupied interdendritic spaces emerging on surface.

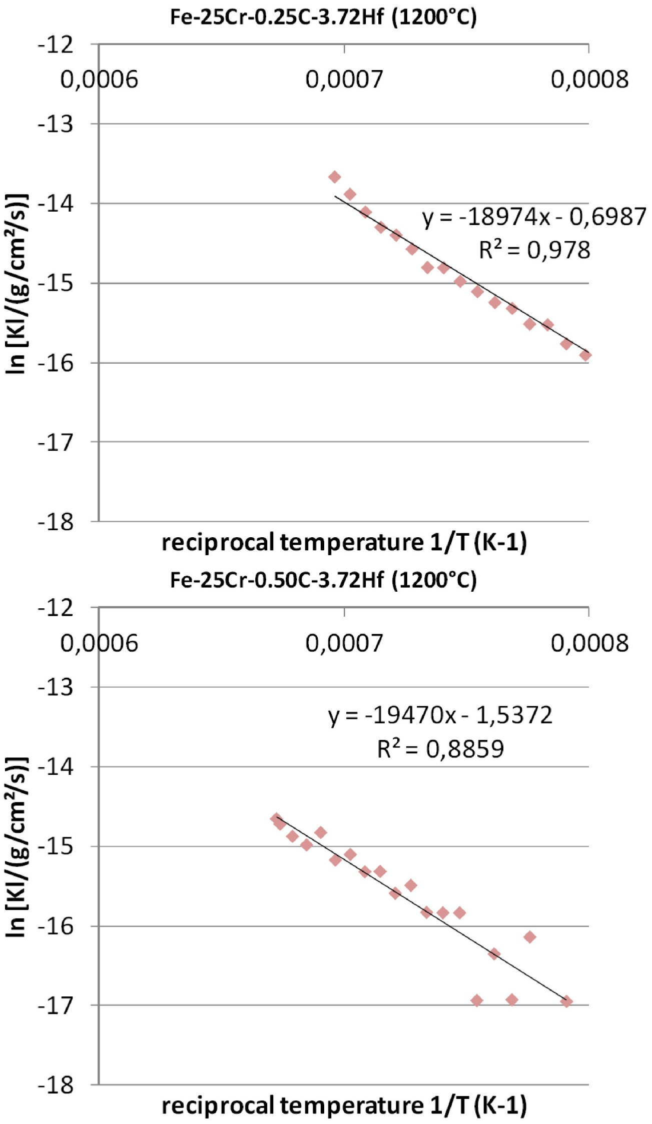

Figure 5 : Arrhenius plot of the linear constant K_l for two of the Hf-containing quaternary alloys

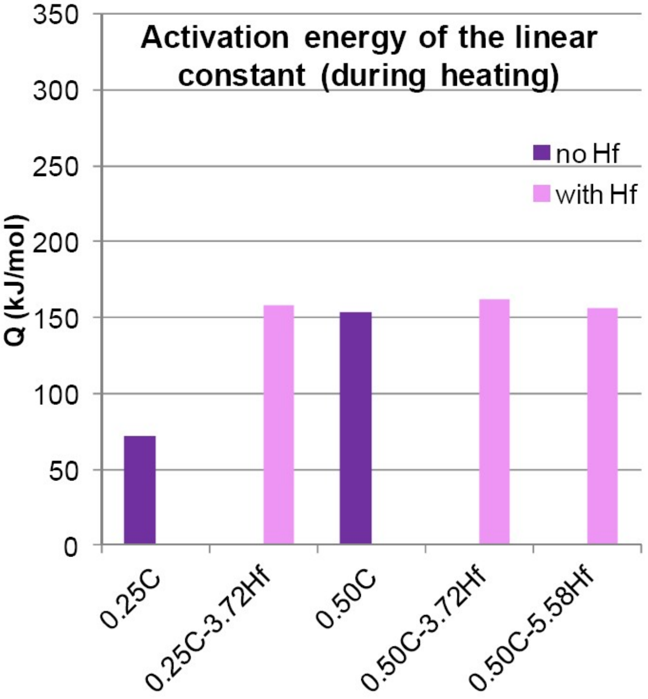

Figure 6 : The activation energies for the linear constant K_l for the five alloys oxidized during the heating

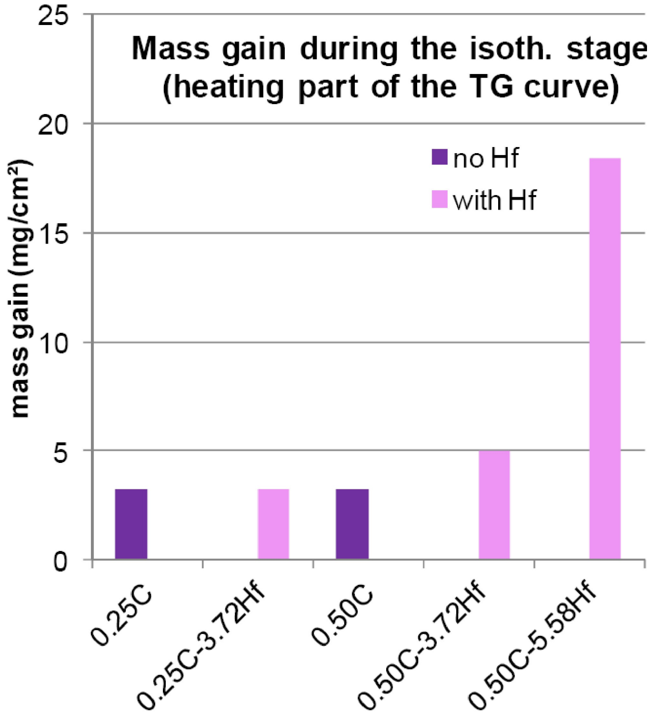

Figure 7 : The total mass gain achieved during the isothermal stage for each of the five alloys (Fe-25wt.%Cr-xC(-yHf))

Isothermal oxidation

The total mass gains obtained only during the isothermal stage were determined on the conventionally plotted mass gain curves ($\Delta m/S = f(t)$). These isothermal thermogravimetry curves were never really parabolic: presence of successive jumps, of linear parts... This reveals that oxidation was not homogeneous all around the samples. However the total mass gain were determined and taken in consideration. The results are presented as histogram again, in Figure 7. One can see that the isothermal mass gain over the 46 hours of stage are very close to one another for four alloys (3 to 5 mg/cm²) while it is five times this value for the Fe-25Cr-0.50C-5.58Hf alloy, this suggesting that the too high Hf content of this alloy disturbed the isothermal high temperature oxidation process.

Oxide spallation at cooling

During the cooling the difference of thermal expansion/retraction between the external oxide and the alloy necessarily induces a progressive compression of the oxide which cannot be entirely relaxed by its visco-plastic deformation, notably when temperature has become too low to allow such nature of deformation. Thus, the oxide often finished to crack and fall: phenomenon called oxide spallation. This can be easily seen on the cooling parts of the curves of mass gain plotted versus temperature as in Figure 1. To characterize this phenomenon for the five iron-based alloys studied here, first the temperature at which the decrease in mass gain finishes to be continuous (due to the continuous increase in Archimede's pressure) to become much more irregular was determined (and graphically given in Figure 8) and the final mass variation after return to room temperature was noted (and graphically given in Figure 9).

Concerning the temperature of oxide spallation start during cooling, it clearly appeared that:

- this temperature decreases (e.i. spallation occurs later) when the carbon content in the alloy (containing Hf or not) increases (Figure 8), and consequently the final mass gain after return to room temperature increases (Figure 9); for a given carbon content this temperature of spallation start is lower for a HfC-containing alloy than for a ternary alloy (Figure 8), and consequently the final mass gain after return to R.T. is higher

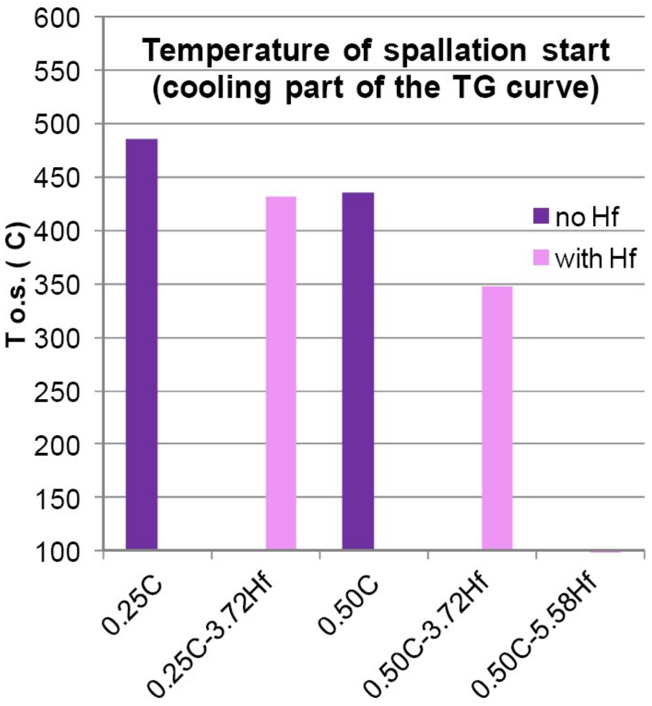

Figure 8 : Temperatures at which the external oxide begins to encounter spallation during the cooling, for each of the five alloys (Fe-25wt.%Cr-xC(-yHf))

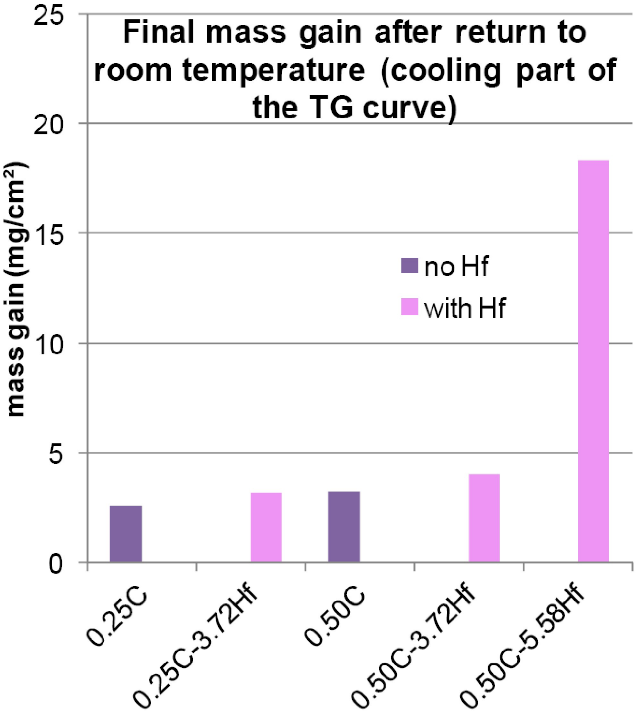

Figure 9 : The final mass gain remaining after complete cooling, for each of the five alloys (Fe-25wt.%Cr-xC(-yHf))

- the 5.58Hf-containing alloy did not know any spallation (Figure 8), and consequently the mass gain after return to R.T. is the most important among the five alloys (Figure 9).

General commentaries

The study of the influence on the high temperature oxidation kinetic aspects during heating, isothermal stage and cooling of the carbon content and of the presence/content of Hf was thus extended here to iron-based alloys with the same carbon contents and similar hafnium contents as for the ternary/quaternary {25wt.%Cr}-containing cobalt-based and nickel-based alloys previously studied[11,12].

Despite that the Hf contents were not exactly the same fir the three Hf-richest alloys of the three families and that the cobalt-based alloys were isothermally oxidized during 50 hours while this stage duration was only 46 hours for the nickel-based and iron-based ones, some comparisons may be done.

Concerning the temperature of oxidation start

The decrease with the alloy's carbon content of this temperature at which mass gain has become high enough to be detected by the thermo-balance was observed for the ternary alloys of the three families; this tends also true for the Hf-containing alloys but there are there several exceptions; however if the Fe-25Cr-0.50C-3.72Hf case is removed this decrease, which is obvious in the Ni-based family, tends to be also true for the Fe-based family while there is apparently no influence in the Co-based family.

Concerning the total mass gain at heating

The increase with the alloy's carbon content of the mass gain achieved during the whole heating is observed for both the ternary Co-based and Co-based alloys, and for the Hf-containing Ni-based alloys; in all the other cases the results are more scattered and no well established rule can be revealed; concerning the effect of hafnium on this same parameter, the results are rather scattered.

Concerning the activation energy of the linear kinetic constant during the heating

Most of the values obtained are in the neighborhood of 150kJ/mol. But there are three exceptions: the Fe-25Cr-0.25C alloy (lower energy) and the two ternary cobalt-based alloys (higher energies); one can notice that these three alloys are the ones which contain the lowest volume fraction of carbides.

Concerning the total mass gain achieved during the isothermal stage

There is no well established rule concerning the effect of the carbon content but in all cases the very high contents in hafnium generally induce higher total mass gains; when the three families are compared to one another, it appears that the greatest mass gains are shown by the cobalt alloys, with or without Hf, while the iron-based alloys and the nickel-based ones led to the lowest isothermal mass gains.

Concerning the temperature of oxide spallation start

It appears that, in presence of hafnium or not, a higher carbon content seems leading to a decrease of the temperature of spallation start (as is to say spallation is delayed to lower temperatures), but there is one exception with the ternary nickel-based alloys; but what was constantly observed is the more or less significant decrease in temperature of spallation start with the presence of hafnium and with its quantity.

Concerning the final mass variation after return to room temperature

The mass variation by comparison with before oxidation test is positive for the iron-based alloys (with or without Hf), the ternary cobalt-based ones and the HfC-containing nickel-based alloys; the ternary nickel alloys had lost mass between before and after oxidation but this was improved by the presence of hafnium in the quaternary ones. Hf also brought improvement to the iron-based alloys while, in contrary, the mass loss was much more important for the cobalt-based alloys with Hf than for the ternary ones, but this was attributed to the very thick multi-composed oxides isothermally formed over these HfC-containing cobalt-based alloys: for so oxidized alloys spallation necessarily induced great mass losses.

CONCLUSIONS

Thus, the presence of hafnium in quantity high enough to generate in the microstructure a new type of interdendritic carbides network potentially allowing a sustainable mechanical reinforcement of highly refractory iron-based alloys to correct their intrinsically low strength, is not detrimental for the high temperature oxidation behavior. This one is globally at a good level, equivalent to the similar nickel-based alloys which can be considered as references in term of performance in resistance against oxidation at high temperature, and of course much better than the similar cobalt-based alloys which displayed the worst behavior, notably concerning isothermal mass gain and oxide spallation. This study of the behavior of iron-based alloys containing HfC carbides will be completed by metallographic characterization of these oxidized samples[13], as this was previously done for the cobalt-based and nickel-based HfC-containing alloys. This will help deeper interpreting the present kinetic effects of high content hafnium or of HfC carbides on the oxidation at 1200°C of iron-based alloys, as well as allow comparisons with the two other families of HfC-containing alloys previously studied, the cobalt-based ones and the nickel-based ones.

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