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Effect of a high hafnium content on the high temperature oxidation of chromium-rich cast alloys. Part 2: Isothermal oxidation and scale spallation of Fe-based alloys

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ABSTRACT

The chromium-rich iron-based alloys, the oxidation behaviour at heating of which was characterized in the first part of this work, were subjected to characterization of their average isothermal oxidation rate as well as of their resistance against oxide spallation during cooling. The isothermal mass gains at 1000°C and 1100°C during 46 hours and the exploitation of the cooling parts of the thermogravimetry curves led to observations about the effect of the high contents in hafnium of these other oxidation parameters. It appeared that the effect of these high amounts in hafnium on the isothermal oxidation was not the same depending on the stage temperature. Concerning their influence on the resistance to scale spallation at cooling from 1000 or 1100°C, the good behaviours of the ternary alloys was not deteriorated by the presence of this element in too high quantities to keep maybe the good behaviour generally observed at lower Hf contents. To summarize, so high Hf contents, which allow developing reinforcing HfC carbides, did not significantly threaten the oxidation behaviour of the alloys, neither during the isothermal oxidation, nor during cooling and probably thermal cycling.

KEYWORDS

Iron-based alloys;
High hafnium contents;
High temperature;
Isothermal oxidation;
Scale spallation at cooling;
Thermogravimetry.

INTRODUCTION

Among the elements which play a beneficial role on the oxidation at high temperature of alloys and superalloys there is hafnium[1]. Concerning especially iron-based alloys, Amano and al[2] have seen that the presence of this element in Fe-20Cr-10Al alloys led to a decrease in oxidation rate at 1200°C, for example. This was also observed by Okabe[3] for Fe-30Cr-4Al between 1000 and 1300°C, who additionally found the presence of HfO_2 inclusions in the alumina scale and who also noticed that a high Hf content improved the scale adherence. The last observation was also done by Jedlinski et al[4] for Fe-23Cr-5Al alloys. Scale adherence was also obviously improved by the presence of hafnium when other elements (as sulphur) threaten scale adherence[5]. Besides what happens in oxidation in hot air, the beneficial influence of Hf in Fe-Cr-Al alloys was also found for such alloys in case of oxidation in hot pure O_2[6].

It seems that there is not so many data about the effect of Hf for iron-based alloys only containing chromium (and no aluminium) in quantity high enough to promote the development of an external chromia scale or of a scale composed of $(Cr,Fe)_2O_3$ with a Cr/Fe ratio varying through the scale or along the scale.

In this work, which follows a first one concerning oxidation at heating[7], the mass gain curves obtained in this former study[7] for cast Fe-25Cr-{0.25 or 0.50C}-{0, 3.72 or 5.58Hf} (wt.%) were exploited again but this time on their isothermal and cooling parts. It was wished to characterize the effect of the presence of hafnium in unusually high quantities on the isothermal oxidation rate and on the behaviour of the external scale during the cooling. The thermogravimetry curves under study are the new ones obtained for stage temperatures equal to 1000 and 1100°C but earlier results obtained for 1200°C[8] were also taken in consideration for enriching the study.

EXPERIMENTAL DETAILS

The alloys of the study

The iron-based alloys of this second part of the study are the same as the ones studied in the first part[7]: they contain a rather high chromium content (25wt.%Cr for all of them), two levels of carbon contents (0.25 and 0.50wt.%), and either no hafnium (ternary alloys for comparison) or two levels of hafnium (3.7 and 5.6wt.%Hf, particularly high by comparison with the usual contents in high temperature alloys). One can remind that these alloys were earlier prepared by foundry from pure elements[9], and that their oxidation behaviour were previously studied in oxidation at 1200°C[8,10]. These results obtained at 1200°C will be added to the ones of the present work to extend the analysis beyond 1100°C. The names of these alloys, and their real chemical composition (obtained by Energy Dispersive Spectrometry) are the following ones:

- "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)

Their as-cast microstructures were already reminded in the first part of this work[7]: an iron-chromium solid solution dendritic matrix, interdendritic spaces containing carbides of two types: hafnium carbides and in some cases chromium carbides in the Hf-containing alloys, but only chromium carbides in the Hf-free alloys.

Thermogravimetry tests and exploitation

One can remind that the five ingots obtained by high frequency induction melting were cut in their centre to provide samples with an almost parallelepiped geometry. These ones were ground with 240-grade SiC papers for smoothing the edges and the corners, then wholly polished with 1200-grade SiC paper (the six faces and the edges and corners again). The thermogravimetry runs were performed with a thermobalance (Setaram TG92), in a continuous flow of dry industrial air.

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, and cooling at -5°C min^{-1}. From the isothermal parts (globally parabolic when the mass gain is plotted versus time) were extracted only the total mass gains due to isothermal oxidation.

The exploitations of the cooling parts of the mass gain files were done following the same procedure as in an earlier work[11]: the mass gains were plotted versus temperature (and not versus time) after correction from the variations of air buoyancy[7]. The following data were deduced from the cooling parts of the obtained new curves:

- temperature at which the curve becomes irregular during cooling (oxide spallation start temperature)
- final mass variation (sometimes positive if no oxide spallation or limited spallation, sometimes negative in case of severe spallation)

RESULTS AND DISCUSSION

The {mass gain versus temperature}-curves:

isothermal part and cooling part

The whole mass gain curves plotted versus temperature are presented in Figure 1 for the {0.25C}-alloy (left) and for the {0.25C-3.72Hf}-alloy (Right), in each case for the three tests (1000 and 1100°C: this work; 1200°C: earlier work[8]). For the Hf-containing alloy one can see that the higher the stage temperature the more important the total isothermal mass gain. This logical order is curiously not true for the Hf-free alloy since the mass gain for 1100°C is higher than the one for 1200°C. For a given stage temperature the total isothermal mass gain appears to be sometimes lower (1000°C), sometimes higher (1100°C) for the Hf-containing alloy than for the Hf-free one (and sometimes equivalent: 1200°C). During the cooling spallation of the external scale occurs only after isothermal oxidation at 1200°C.

The analogous curves but obtained for the three other alloys are presented in Figure 2: {0.50C}-alloy (left), the {0.50C-3.72Hf}-alloy (middle) and the {0.50C-5.58Hf}-alloy (Right). Concerning the isothermal mass gain curves there is now curious order in three cases: as for the {0.25C, Hf-free}-alloy the isothermal mass gain for the {0.50C, Hf-free}-alloy for 1100°C

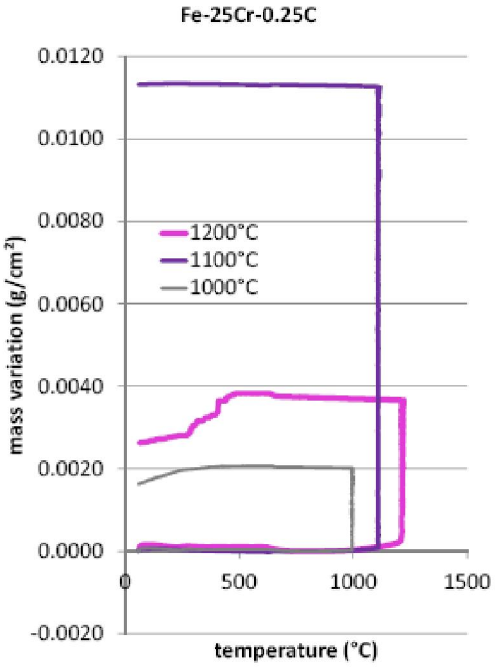

Figure 1 : The whole mass gain curves plotted versus temperature (after correction from the air buoyancy variations[7]) in the case of the two {0.25wt.%C}-containing alloys

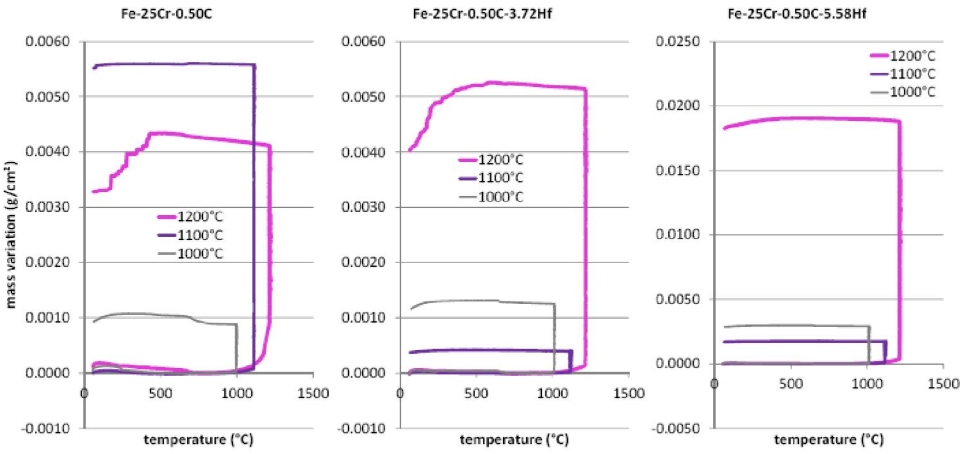

Figure 2 : The whole mass gain curves plotted versus temperature (after correction from the air buoyancy variations[7]) in the case of the three {0.50wt.%C}-containing alloys

is higher than for 1200°C and, for the two Hf-containing alloys, this isothermal mass gain is higher for 1000°C than for 1100°C. It also tends to increase with the presence of Hf and with the Hf content for 1000°C and 1200°C while there is seemingly no real difference between the two Hf-containing alloys for 1100°C. In contrast the isothermal mass gain is much more important for the Hf-free alloy at this same temperature.

Temperatures of oxidation start

On the previous graphs presented in Figure 1 and Figure 2, one can specify for all the three curves plotted together in each of them, the mass gains obtained during the 46 hours of isothermal stage (no participation of the oxidation during heating). The results, which are graphically presented in Figure 3, confirm what appeared on the mass gain curves in Figure 1 and Figure 2 and which was already commented above. Globally the addition of hafnium tends to diminish the oxidation of the {0.25C}-containing alloy but, in contrast, it enhance oxidation when the carbon content is double (0.50C).

Oxide spallation at cooling

After the isothermal stage a cooling at -5°C/min was applied for all the samples. The cooling of the metallic alloys induces a thermal retraction which is generally more important than the one of the external oxide. This induces compressive stresses in the scale which may lead to rupture and detachment from the metallic substrate (the alloy). One already saw above on the whole mass gain curves plotted versus temperature that irregularities occurred on the curve in some cases (here: all curves after isothermal stage at 1200°C). This happens then at a temperature which is to be considered as being a first parameter characterizing the oxide spallation. The results are presented in the histogram shown in Figure 4. Since spallation did not occur during the cooling down to room temperature for the samples which were just before isothermally oxidized at 1000 and 1100°C, only the results for 1200°C are available. One can see that the presence of hafnium (3.72wt.% targeted, 3.5 to 3.9wt.% obtained) delayed spallation start to lower temperatures for the {0.25C}-alloys and the {0.50C}-alloys while a higher Hf content (5.58wt.% targeted, 4.9wt.% obtained) allowed suppressing spal-

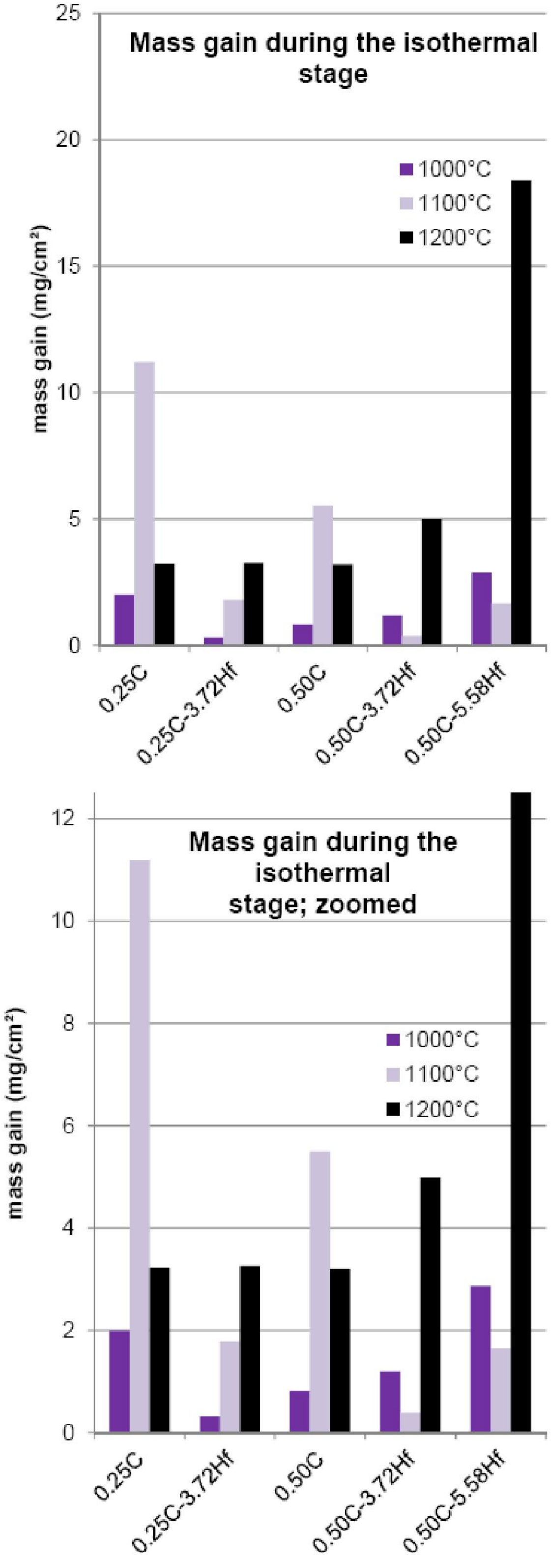

Figure 3 : Histogram presenting for the five alloys the values of the total mass gain achieved during the isothermal stage (exclusively) realized at either 1000 or 1100°C (this study); the ones previously obtained for 1200°C in an earlier work[8] are also added

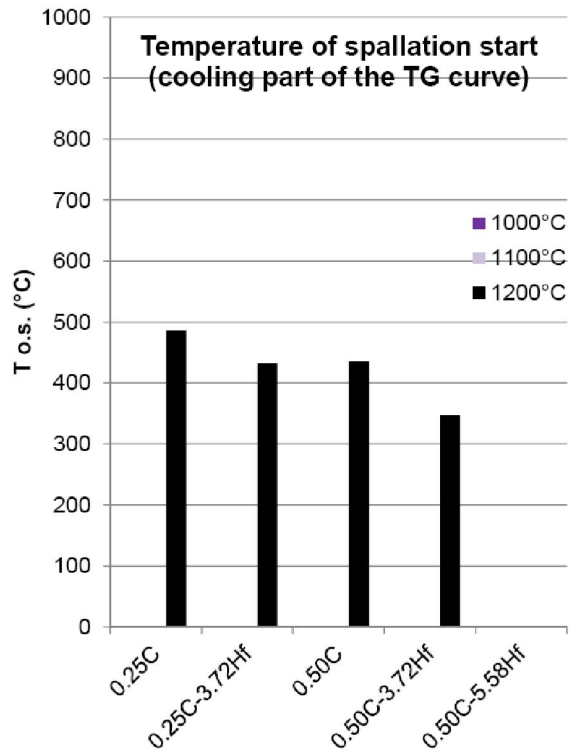

Figure 4 : Histogram presenting the values of the temperature of spallation start during the cooling, for the five alloys, after isothermal stage realized at 1000 or 1100°C (this study), and also at 1200°C (previous study[9]); spallation for only the four first alloys after isothermal oxidation at 1200°C

lation at cooling from 1200°C. One may also note that a higher content in carbon seems to delay the spallation start too, in absence of hafnium or in its presence.

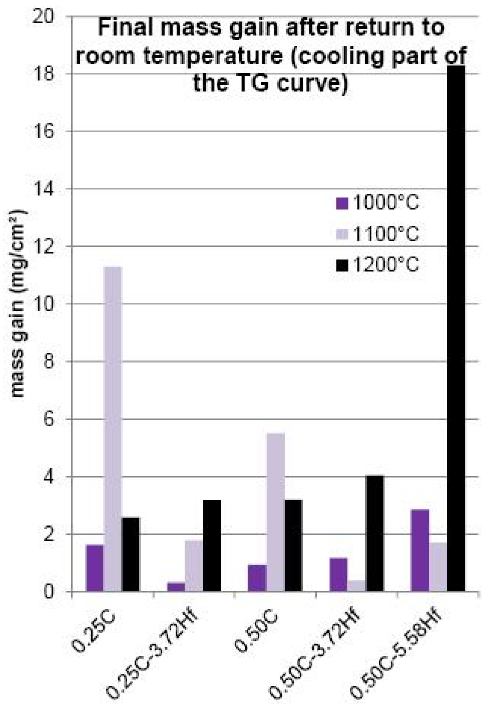

Figure 5 : Histogram presenting the values of final mass gain at the end of cooling, for the five alloys after isothermal oxidation at 1000 or 1100°C (this study), and also at 1200°C (previous study[9])

The final mass gain after return to room temperature (Figure 5) is generally not different from what was obtained for the isothermal mass gains (Figure 3). The values for 1200°C are, for some of them, a little decreased, this being due to spallation during cooling.

The surface aspects of the oxidized samples are illustrated by the scanned images (office scanner) displayed in Figure 6. These images confirm that no spallation occurred during cooling for all these samples. The

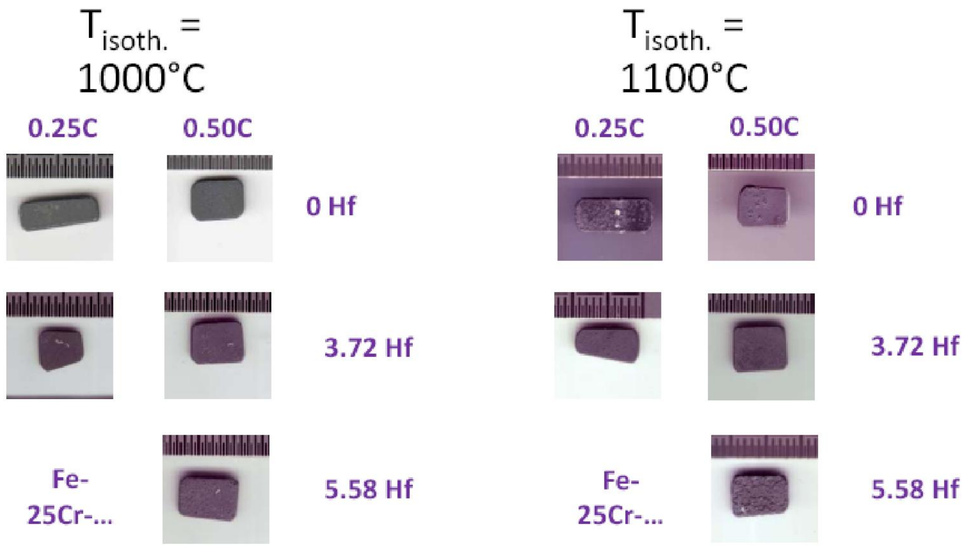

Figure 6 : Surface aspects of the oxidized samples after cooling down to room temperature from 1000 or 1100°C (temperatures of isothermal oxidation); images issued from scanning using an office scanner

small areas of denuded alloy are due to oxide detachment during the room temperature manipulation of the oxidized samples.

General commentaries

With such especially high hafnium contents it appeared that the Hf-containind alloys tend to isothermally oxidize faster than the Hf-free ones. This is particularly obvious for the two extreme temperatures 1000°C (this study) and 1200°C (earlier work[7]). The results obtained for 1100°C, which were rather scattered when considered versus temperature, seem showing an inversed effect: decrease in oxidation rate, much more in good agreement with literature (which concerns – it is true – much lower Hf contents). In contrast, the well-known effect of hafnium on the resistance of iron-based alloys against oxide spallation was not denied here: it probably exists even for such high Hf contents. Indeed there is no spallation during cooling from the stage temperature, neither from 1000°C nor from 1100°C. It is true that the Hf-free alloys did not themselves suffer of scale spallation during cooling, but high Hf contents at least did not promote spallation. On the contrary it was seen earlier[7] that spallation occurred for cooling from 1200°C after 46 hours of oxidation at this temperature, for the same alloys, but even in these cases Hf demonstrated a beneficial effect since the temperature of spallation start was shifted downwards.

CONCLUSIONS

Thus, it was seen, in this second part of this work, that the cooling parts of the thermogravimetry curves were of interest again: no visible irregularities showing oxide spallation during cooling from the concerned stage temperatures. Even if present with the high amounts necessary for obtaining HfC carbides in the microstructure for alloy strengthening purpose, hafnium leads to maintain a good resistance against spallation. Unfortunately it was also found that the isothermal oxidation rate was globally not lowered by the presence of hafnium. This appeared true for 1100°C but not at the other temperatures. The beneficial effect of hafnium in this field seems to be limited to the usual low Hf contents generally added to the alloys.

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