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

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ABSTRACT

Hafnium is one of the most important elements for favouring the high temperature oxidation resistance of alloys and superalloys when present in low quantity. It may also lead to the development of interdendritic eutectic HfC carbides in cobalt alloys when several weight percents are added to their compositions. Such carbides are especially stable at high temperature and then potentially very efficient for the mechanical resistance at high temperature. Three alloys strengthened by eutectic HfC carbides were tested for 50 hours in oxidation at 1200°C in synthetic air with thermogravimetry measurements. The mass gains recorded during the heating, the isothermal high temperature stage and during the cooling were all analyzed and the results compared with the ones obtained with ternary Co-Cr-C alloys with the same chromium and carbon contents, in the same operating conditions. It appeared that hafnium strongly influences the oxidation kinetic during heating and during the isothermal stage, as well as concerning the oxide spallation at cooling. The effects of so high hafnium contents are either beneficial or detrimental for the high temperature oxidation behaviour, this depending on the criterion followed.

KEYWORDS

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

INTRODUCTION

High temperature applications generally require, for the materials that one envisages to use, high level of several properties in the mechanical field as well as in the chemical one. When the materials are metallic the alloy family which is generally considered is the one of the superalloys. The most classical of these alloys may be nickel-based, {nickel, iron}-based or cobalt-based[1]. The latter family is mainly constituted of cast alloys strengthened by carbides[2], even if there are also many cobalt-based alloys elaborated following different ways and/or solid-solution strengthened, for example.

The ones among the carbides-strengthened cobalt-based superalloys which are considered for very high temperature uses, notably for higher than 1000°C, must be strengthened by carbides especially stable at high temperature. This is the case of tantalum carbides[3], but other MC carbides may be more efficient in this field[4]. This is the case of the hafnium carbides, which can be moreover obtained with similar "script-like" features as for the tantalum carbides which form a eutectic with matrix allowing therefore a good attachment of the neighbour matrix dendrites to one another. However the behaviour in high temperature oxidation of such cobalt-based alloys containing HfC carbides remains to be better known. More precisely, if the isothermal oxidation kinetics of similar alloys were previously characterized (e.g.[5]), the oxidation start at heating as well as the spallation at cooling were rarely studied. This can be of great interest since hafnium, which is known as playing an important role in high temperature oxidation when present in small quantities in refractory alloys[6], probably much more influence this behaviour when it is present in much greater quantities in the chemical composition.

The purpose of the present work is to explore the behaviour in oxidation at high temperature – essentially during heating and cooling (respectively before and after) an isothermal stage – of HfC-strengthened chromium-rich cobalt alloys containing various carbon and hafnium contents, previously elaborated and characterized about their as-cast microstructures and hardness[7].

EXPERIMENTAL DETAILS

The alloys of the study

One can remind[7] that three HfC-strengthened cobalt-based alloys were elaborated from pure elements (Co, Cr, Hf and C) by High Frequency Induction melting under an inert atmosphere of argon. They solidified in the water-cooled copper crucible of the HF furnace and ingots of about 40g of polycrystalline equi-axed alloys were obtained. Their "{targeted composition}-names" and their obtained chemical compositions as measured by Energy Dispersive Spectrometry (EDS, device equipping the JEOL JSM-6010LA) were:

- "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)

In parallel four Co-25wt.%C-xC (with x=0, 0.25, 0.50, and 1.00wt.%) alloys were also synthesized following the same elaboration way to compare hardnesses. Here only the two alloys with the same targeted contents in carbon as the previous Hf-containing alloys were considered for comparison:

- "Co-25Cr-0.25C": 24.22wt.% Cr (Co: bal., C: not measured)
- "Co-25Cr-0.50C": 23.79wt.% Cr (Co: bal., C: not measured)

Preparation of the samples for the thermogravimetry tests

In each of the {3 + 2} ingots an almost parallelepipedic sample was cut near the centre of the ingot, to avoid the most external zone enriched in pro-eutectic HfC carbides and then to be sure to have chemically and microstructurally homogeneous samples. They were polished with 240-grit SiC papers to smooth the edges and corners, and finished with 1200-grit SiC papers for the main faces (a well as edges and corners again. The thermogravimetry runs were performed in artificial air ($80\%N_2$-$20\%O_2$) in a Setaram TG92 thermobalance. The heating rate from ambient temperature was 20°C min^{-1}, the isothermal (1200°C in all cases) stage duration was 50 hours, and the cooling rate was -5°C min^{-1}. The exploitations of the mass gain files for the heating part and for the cooling part were realized following the same procedures as earlier presented respectively in[8,9] and in[10,11].

RESULTS AND DISCUSSION

Initial microstructures of the alloys

We can remind that the three Hf-containing alloys are composed of a dendritic matrix of cobalt-based solid solution and of mainly hafnium carbides (example of microstructure given in Figure 1). These ones are essentially "script-like" eutectic carbides present in the interdendritic areas, mixed with matrix. However, additional HfC compact particles (suspected to be pro-eutectic carbides) are also present in the carbon-lowest alloy (Co-25Cr-0.25C-3.72Hf) and in the hafnium-highest alloy (Co-25Cr-0.50C-7.44Hf), which both do not contain other types of carbides, while chromium carbides can be seen in the third Hf-containing alloy (Co-25Cr-0.50C-3.72Hf) in some interdendritic locations, in addition to the eutectic HfC carbides.

The two ternary Co-25Cr-xC alloys added to the study for comparison, also display a dendritic cobalt-based matrix. In contrast with the previous quaternary alloys they contain only interdendritic chromium carbides, rather rare in the Co-25Cr-0.25C alloy and more visible in the Co-25Cr-0.50C one.

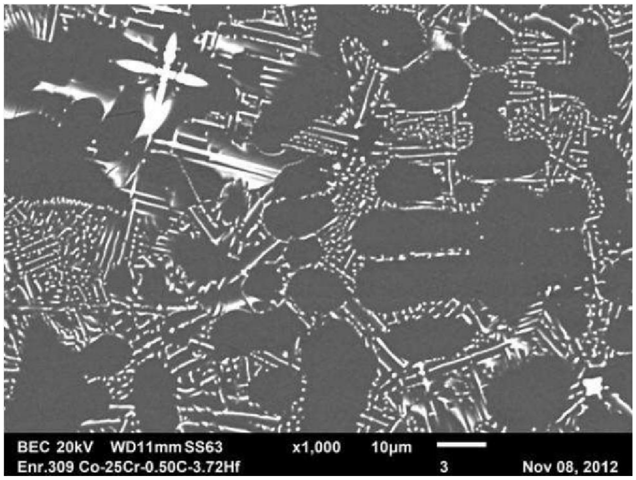

Figure 1 : Example of as-cast microstructure of a HfC-strengthened alloy (here: Co-25Cr-0.5C-7.44Hf alloy)

Exploitation of the obtained mass gain curves

Only four mass gain curves out of the five ones were really exploitable since a problem occurred during the thermogravimetry test of the Co-25Cr-0.50C alloy (only the earlier part of the mass gain curve is available, as well as the major part of the cooling). The five curves were analyzed to specify the temperature of oxidation start (as defined as being the one corresponding to the earlier detection of mass gain after correction from the air buoyancy[8,9]), as well as the total mass gain achieved during heating before reaching the isothermal stage. The mass gain files were thereafter exploited to value the isothermal mass gain and to see if spallation occurred during cooling. An example of the $\{\Delta m/S = f(T)\}$ curves considered for these different determinations is given in Figure 2.

Results: Oxidation at heating

These mass gain curves were analyzed in order to determine first the temperature at which the mass gain became perceptible to allow detecting a real oxidation (Figure 3). It seems that the presence of hafnium carbides favours a lower temperature of oxidation start (comparison of on the one hand the Hf-free ternary alloys, and on the other hand the Hf-containing quaternary alloys) while the presence of additional chromium carbides tends to have the opposite effect (oxidation start temperature lower for the Co-25Cr-0.50C and Co-25Cr-0.50C-3.72Hf alloys than respectively for the Co-25Cr-0.25C one and for the two other Hf-containing ones).

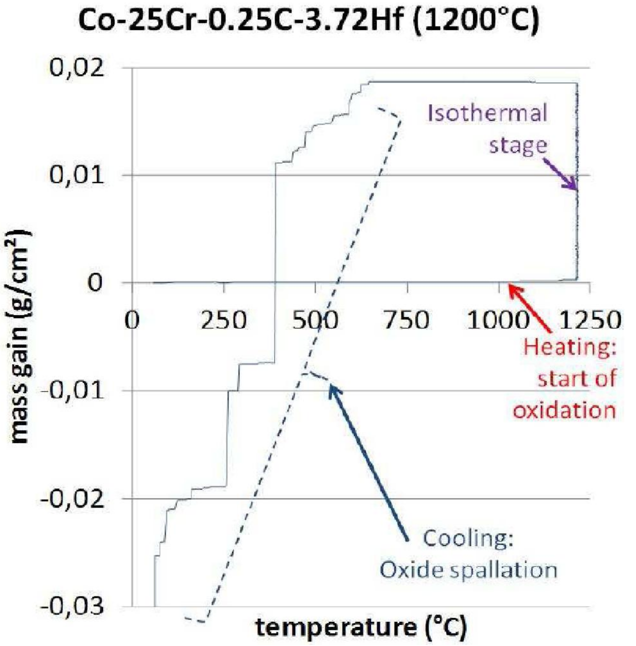

Figure 2 : Example of a mass gain curve plotted versus temperature instead versus time

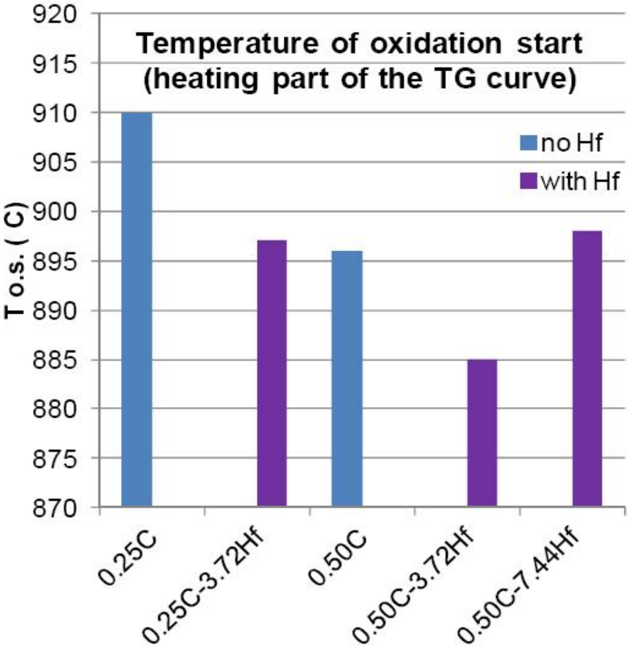

Figure 3 : Temperatures at which the mass gain due to real oxidation became detectable by the thermo-balance during the heating, for each of the five alloys (Co-25wt.%Cr-xC-(yHf))

The same mass gain curves lead to the values of the total mass gain obtained during the whole heating plotted in Figure 4 as histogram too. The oxidation during heating appears to be significantly higher for the HfC-free ternary alloys than for the HfC-containing ones. Thus, in presence of hafnium, the oxidation seems starting sooner but the oxidation rate quantified by the measured mass gain is lower after.

In order to better describe the oxidation rate during heating we decided to calculate, for each temperature during the heating, the value of the kinetic linear constant expressed by:

$$K_l(T_n) = [(\Delta m/S)_{n+1} - (\Delta m/S)_n] / (T_{n+1} - T_n)$$

where n is the number of the running recording step, T_n the corresponding value and $(\Delta m/S)_n$ the corresponding mass gain per surface unit area (always after correction from the air buoyancy).

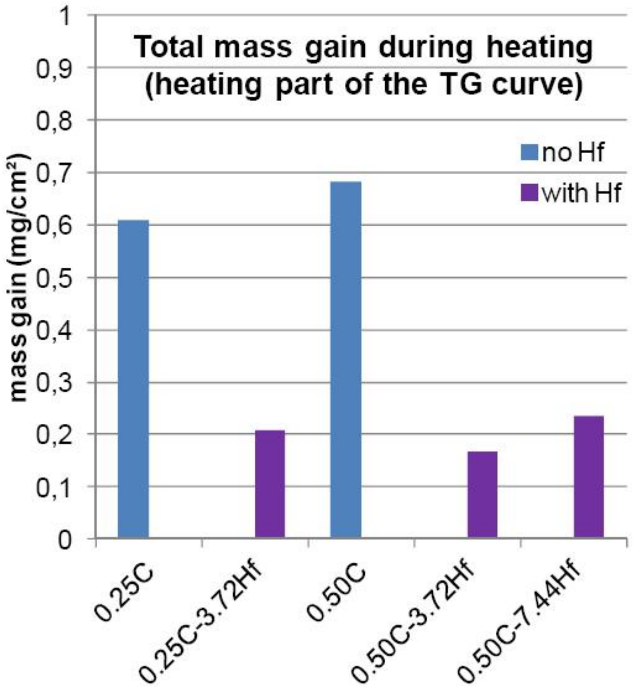

Figure 4 : The total mass gain achieved during the heating, for each of the five alloys (Co-25wt.%Cr-xC(-yHf))

The variation of $K_l(T)$ with the temperature T was plotted in the Arrhenius scheme for the two Hf-free ternary alloys in Figure 5 and for the three Hf-containing quaternary alloys in Figure 6, in all cases for T varying over the temperature range delimited by the temperature of oxidation start of the alloy (as defined above) and the stage temperature (1200°C). It appears that in all cases the obtained graph is rather close to a straight line. The values of K_l at temperatures near 1200°C (the fastest linear mass gain at these highest temperatures) are much higher for the Hf-free alloys than for the Hf-containing ones, this explaining the higher mass gains achieved during the heating for the Hf-free alloys than for the Hf-containing ones. The slopes of these straight lines were then determined, and the corresponding activation energies calculated.

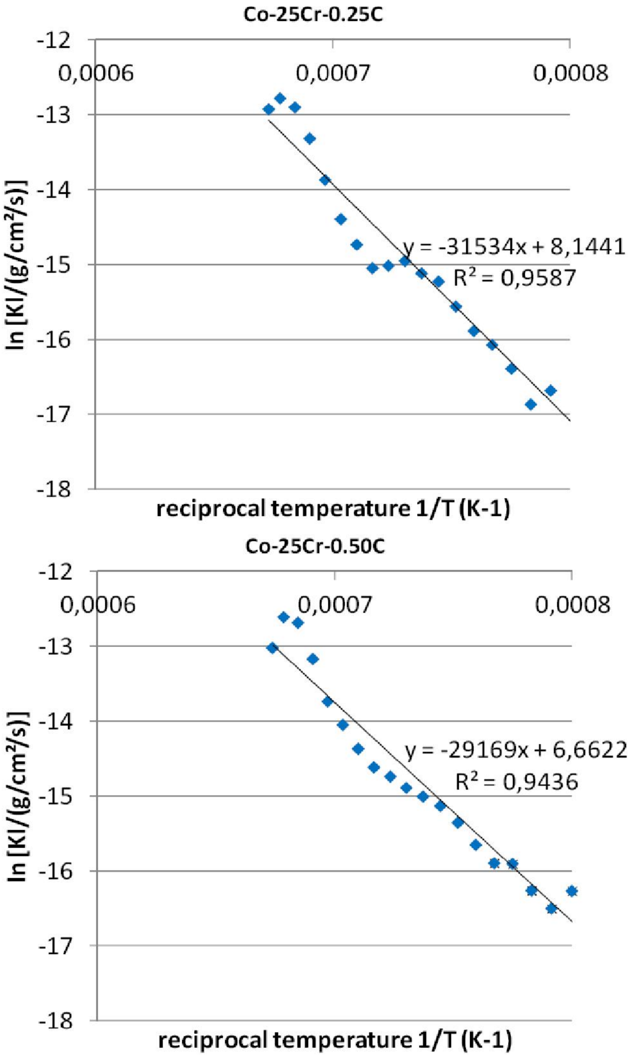

Figure 5 : Arrhenius plot of the linear constant K_l for the two Hf-free ternary alloys

The latter ones are graphically displayed in Figure 7. The activation energy appears being higher for the Hf-free alloys than for the Hf-containing ones, this revealing that the oxidation mechanisms are probably not the same.

Results: Isothermal oxidation

The isothermal mass gain curves of the three Hf-containing alloys are globally parabolic but the kinetic is very high, much faster than for the two Hf-free alloys during the first half of the isothermal stage during which their kinetics are also parabolic but characterized by much lower values of parabolic constants (about 10 or 20 times lower). In contrast the oxidation kinetic of the Co-25Cr-0.25C alloy loses its parabolic character after about 25 hours, with a mass gain becoming linear and fast. The second half of the mass gain of the Co-25Cr-0.50C alloy is not available, this being due to a problem which did not allow continuing to record the mass gain (however the correct value obtained at the beginning of the cooling was taken for the graph). These isothermal kinetic differences can be found in Figure 8 which shows the variation of the total mass gain achieved during the whole isothermal stage: because of their fast parabolic mass gains the three Hf-containing alloys led to final mass gains especially important since they are even higher than the one of the Co-25Cr-0.25C alloy despite its linear oxidation during the second half of its isothermal stage.

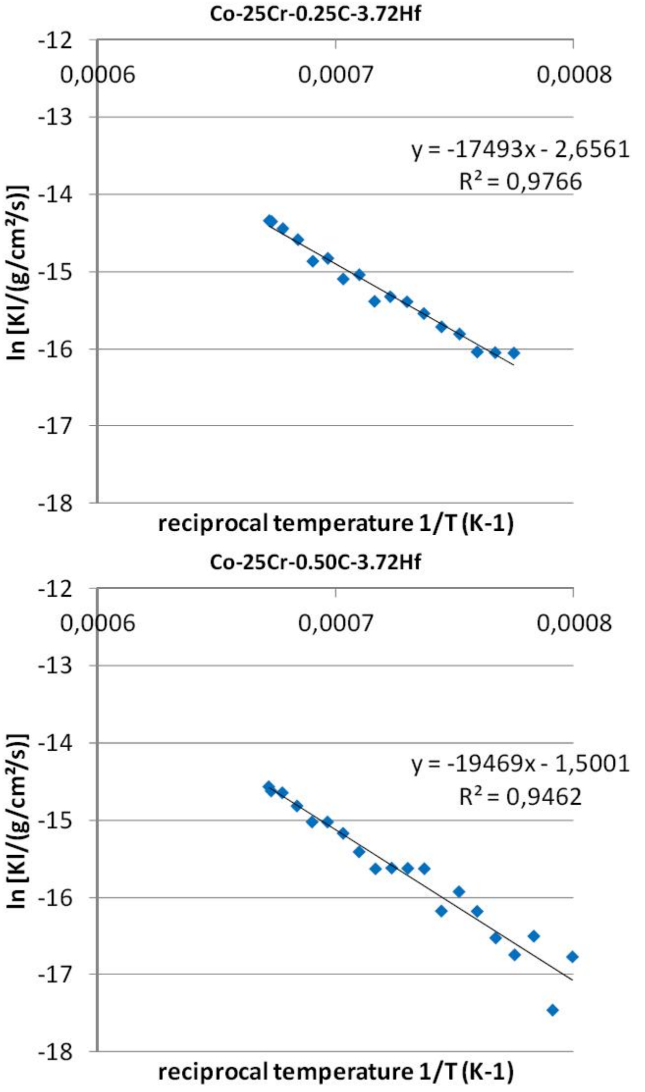

Figure 6 : Arrhenius plot of the linear constant K_l for two of the Hf-containing quaternary alloys

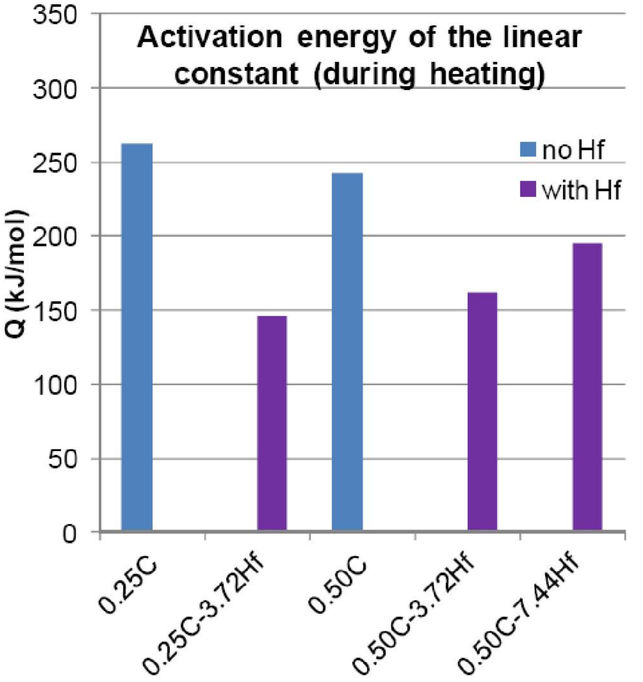

Figure 7 : The activation energies for the linear constant K_l for the five alloys oxidized during the heating

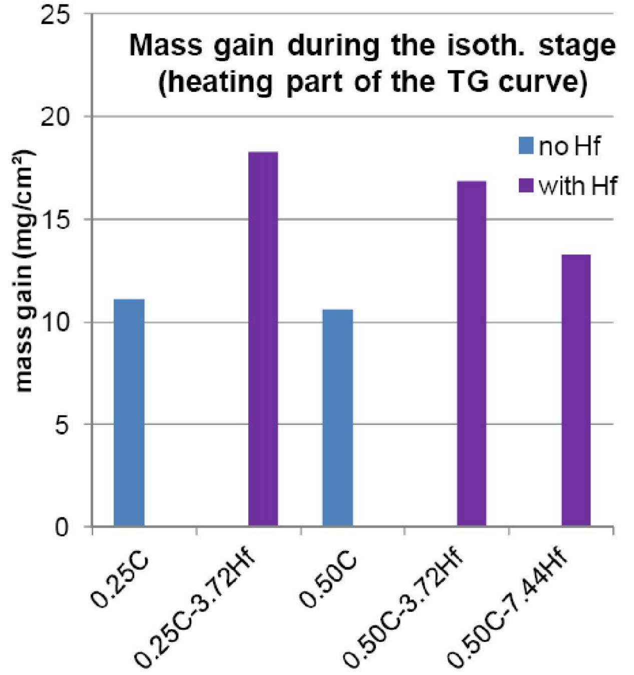

Figure 8 : The total mass gain achieved during the heating for each of the five alloys (Co-25wt.%Cr-xC(-yHf))

Results: Oxide spallation at cooling

When the cooling occurs at the end of the isothermal stage the temperature of both oxide and alloy decreases with as consequence a thermal contraction which is more important for the metallic substrate than for the oxide layer. The latter is then submitted to compressive stresses which are not totally compensated by visco-plastic deformation of the oxide (possible at so high temperature) and the scale finishes breaking, with consequently a loss of oxide visible on the cooling part of the thermogravimetry curve (very irregular decrease in mass). The temperatures at which the phenomenon occurred for the five alloys during the cooling are represented in Figure 9, on which one can see that oxide spallation occurs during the cooling sooner (e.i. at higher temperature) for the Hf-free alloys than for the Hf-containing ones, and seemingly also for a higher carbide density in the two cases. It seems therefore that Hf delayed the loss of external oxide as well as a great quantity of carbides: better properties of the oxide formed? better adherence of the oxide on the substrate? thermal contraction of alloys reduced by a high density of carbides?

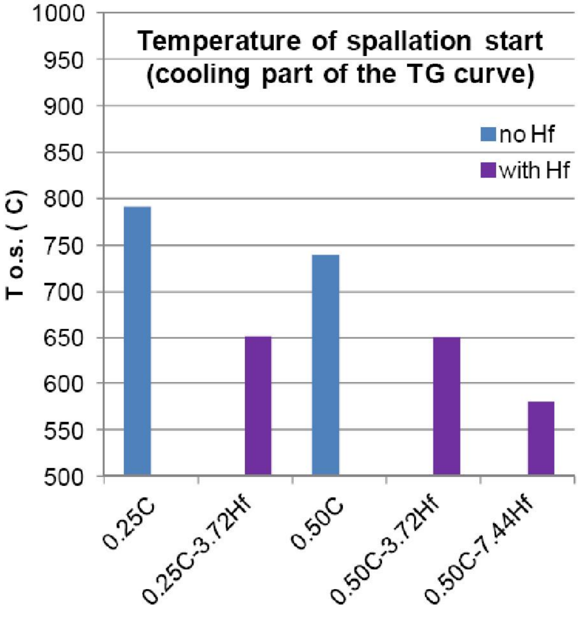

Figure 9 : Temperatures at which the external oxide begins to encounter spallation during the cooling, for each of the five alloys (Co-25wt.%Cr-xC(-yHf))

The final mass variations after return to room temperature are graphically given in Figure 10. The mass loss is particularly high for two of the Hf-containing alloys while the balance remains slightly positive for the three alloys containing exclusively (Co-25Cr-0.25C and Co-25Cr-0.50C) or partly (Co-25Cr-0.50C -3.72Hf) chromium carbides.

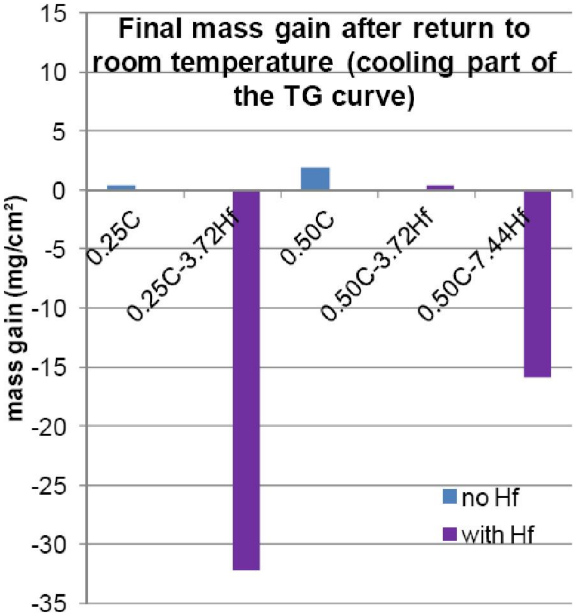

Figure 10 : The final mass gain remaining after complete cooling, for each of the five alloys (Co-25wt.%Cr-xC(-yHf))

General commentaries

The comparative study of high temperature oxidation of cobalt alloys containing hafnium carbides and of other alloys containing only chromium carbides led to significantly different behaviours during the heating, the isothermal stage and the cooling (oxide spallation). Two antagonist influences were observed above during the heating: a tendency to have oxidation start temperatures higher for the Co-Cr-C alloys than for the Co-Cr-C-Hf ones (which appear then to be more sensible to oxidation) and in contrast a higher mass gain achieved during the whole heating not for the Co-Cr-C-Hf alloys despite they started oxidizing sooner but for the Co-Cr-C ones which started oxidizing at high temperature but seemingly faster after. The investigation about the oxidation rates during the heating was pursued by analyze of the linear constants which brought first explanations to the previous observations. These ones have to be obviously classified in two categories: a high level for the Co-Cr-C alloys (about 250kJ/Mol) and a low level (around 165kJ/mol), with, as for the oxidation start temperature and the heating mass gain, a possible influence of the carbon content e.i. of the carbides density. The effects of the presence of Hf and of the carbide density need future investigations to be really explained.

During the isothermal stage the hierarchy between the Hf-free alloys and the Hf-containing ones is inversed by comparison with the oxidation during heating: although the mass gains during heating were higher for the Co-Cr-C alloys than for the Co-Cr-C-Hf ones, the latter alloys isothermally oxidized much faster than the ternary alloys. The examination of the corrosion products formed on the surface (compactness, porosity quality, multiplicity of the external oxides …) will potentially bring interpretations and explanations for these kinetic differences.

The easiness of oxide spallation as well as the amount of mass losses are also deeply dependent on the Hf presence and of the carbide density. One can guess that Hf acts as a favorable element for the adherence of the external oxide – for these especially high contents as for the more usual lower contents (for which such effect is often evocated) – but one can also remind that carbon (which directly governs the carbide density) as well as hafnium (which is a particularly strong carbide-former element) led to more numerous interdendritic carbides, the low thermal expansion (or contraction) of which may reduce the alloy one, allowing a better accommodation with the low average thermal contraction coefficient of the external oxide, with as consequence lower compressive stresses applied to the later. One can imagine that the critical compressive stress is then reached at lower temperatures. Concerning the mass loss by spallation which is much greater for the Co-Cr-C-Hf alloys than for the Co-Cr-C ones, this is easily explainable if one remind that the isothermal mass gain kinetic was much higher for the former alloys than for the later ones: when spallation finally occurred for the Co-Cr-C-Hf much more oxides are lost, by comparison with the Co-Cr-C alloys.

CONCLUSIONS

The unusually high quantities of hafnium added to the chemical composition of the studied cobalt alloys led to significant changes in their oxidation behavior. The influence of Hf is sometimes beneficial and sometimes detrimental. This was first seen here on the thermogravimetry records but complementary explanations can be expected by the examination of the external oxides and of the sub-surface states of the oxidized samples. The presentation of metallographic results is precisely the objectives of the second part of this work[12].

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