Effect of a high hafnium content on the high temperature oxidation of chromium-rich cast alloys. Part 6: Isothermal oxidation and scale spallation of Co-based alloys

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ABSTRACT

The cooling parts of the mass gain curves of chromium-rich cobalt-based alloys, the oxidation behaviours of which were studied during heating up to 1000 or 1100°C in the first part of this work, were analysed in terms of average isothermal oxidation rate and resistance against oxide spallation. It was found that the presence of 4 to 8 wt.% of hafnium was slightly detrimental for the isothermal oxidation behaviour since the mass gain rates were more or less higher than for the hafnium-free ternary alloys added to the work for comparison. In contrast, the gainful effect on the resistance to oxide spallation at cooling was systematically observed. As for the analogous iron-based and nickel-based alloys earlier studied in the same conditions, hafnium demonstrated its beneficial effect in this field. For the isothermal oxidation a critical Hf content under which Hf is gainful and beyond which it becomes deleterious, is proposed.   © 2015 Trade Science Inc. - INDIA

INTRODUCTION

Among the reactive elements allowing improvements of superalloys in high temperature oxidation behaviour, hafnium appears as particularly important[1]. This element is used for nickel-based alloys, iron-based alloys and also cobalt-based alloys. In the later alloy's family Hf may be added to bulk alloys[2] as well as to metallic coatings[3], during the elaboration by foundry or other means, as well as through ion implantation[4]. Introduced with contents near 1wt.% it may improve the oxidation rate as found for example by Stringer *et al*[2] in the case of Co-

Cr-Al alloys oxidized between 1000 and 1200°C in air. These authors also observed improvements of the oxidation resistance in thermal cycling, due to less than 1.5 wt.%., and they claimed that hafnium was, in their case, even slightly more efficient than yttrium, another well-known element able to considerably favour scale adhesion by a pegging mechanism. Such effect of hafnium was also wished and obtained by Song et *al*[3] for CoNiCrAl alloys serving as bond coats deposited on superalloys before depositing TBC (thermal barrier coatings). Improvements of the adherences of oxide scales were also obtained by Provenzano *et al*[4] for another cobalt alloy, a Co-22Cr-11Al coating.

Generally introduced in alloys in low quantities (around

1 wt.% and often less), Hf is rarely added to reach several percents. Some works concerned higher contents in Hf in cobalt alloys as in a study of Voitovich *et al*[5] dealing with the high temperature oxidation of binary Hf-Co alloys, but they are not numerous. Being a strong carbide-former elements, Hf can be present in several weight percents in the chemical composition of chromium-rich cast alloys as the same time as carbon, in order to develop a strengthening interdendritic network of HfC carbides which are very stable at high temperature[6]. The presence of so high quantities of hafnium for a high temperature mechanical purpose may influence the behaviour of the concerned alloys in oxidation at high temperature, and notably concerning what occurs during thermal cycling which favours oxide scales detachments. In order to verify if hafnium, when introduced to reinforce cobalt alloys with carbides, keeps its beneficial effect on scale adhesion, one has here characterized the resistance of three Hf-rich HfC-reinforced chromia-forming cobalt-based alloys against spallation during the cooling which follows a 50 hours-long isothermal oxidation stage, and compared the behaviours of these alloys with the ones of Hf-freee ternary alloys having the same chemical composition as the three first alloys, hafnium excepted.

EXPERIMENTAL DETAILS

The alloys of the study

The cobalt-based alloys considered in this second part of a study the first part of which concerned the effect of hafnium on the oxidation during heating[7], all contain 25wt.%Cr, two levels of carbon contents (0.25 and 0.50wt.%). Two alloys were simply ternary alloys but three other alloys contained two levels of hafnium (3.7 and 7.4wt.%Hf). One can remind that these alloys were earlier prepared by foundry from pure elements[8], and that their oxidation behaviour were previously studied in oxidation at 1200°C[9,10]. 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:

- "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 as-cast microstructures were already reminded in the first part of this work[7]: a cobalt-chromium solid solution dendritic matrix, interdendritic 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 50 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)

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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 hand) and for the {0.25C-3.72Hf}-alloy (right hand), in each case for the three tests (1000 and 1100°C: this work; 1200°C: earlier work[9]). One can see first that the isothermal mass gain is logically more important for a higher temperature, in both cases. Second it seems that the cooling parts are rather irregular.

The analogous curves but obtained for the three other alloys are presented in Figure 2: {0.50C}-alloy (left hand), the {0.50C-3.72Hf}-alloy (middle) and the {0.50C-7.44Hf}-alloy (right hand). The same general comments as done above for the {0.25C}-alloys can be applied at these curves: for a given alloy the higher the temperature, the more important mass gain during the isothermal stage, and cooling parts of the curves generally irregular.

Mass gain during the isothermal stage

At all temperatures but especially at 1100 (and 1200°C[9]), the Hf-containing alloy oxidized faster than the ternary one, with a final isothermal mass gain for the {0.25C-3.72Hf}-alloy equal to twice the {0.25C}-

alloy's one. The same tendency to have a globally faster isothermal oxidation than the Hf-free {0.50C}-alloy can be noticed for the {0.50C-3.72 or 7.44Hf}-alloys, but not in the same proportions as the {0.25C}-alloys. This first feeling is confirmed when one has a look at Figure 3 in which the total mass gains obtained during the isothermal stage are graphically presented by a histogram. Indeed, as previously seen for 1200°C[9], the isothermal mass gain is generally higher in presence of hafnium for a given carbon content, at 1000°C as well at 1100°C. In contrast, by considering separately the ternary alloys on one hand and the Hf-containing alloys on the other hand, the carbon content does not have a significant and reproducible influence.

Oxide spallation at cooling

After the isothermal stage a cooling at -5°C/min was applied for all the samples. The first criterion which was studied is the temperature at which the cooling part of the thermogravimetric curve became irregular, revealing a start of loss of external oxide. The results are presented in a second histogram, in Figure 4. One can see first that cooling from the 1100°C isothermal stage temperature led to a spallation beginning occurring for the Hf-containing alloys at a temperature lower than for the ternary alloys with the same carbon content. This appears evident by comparing the spallation start
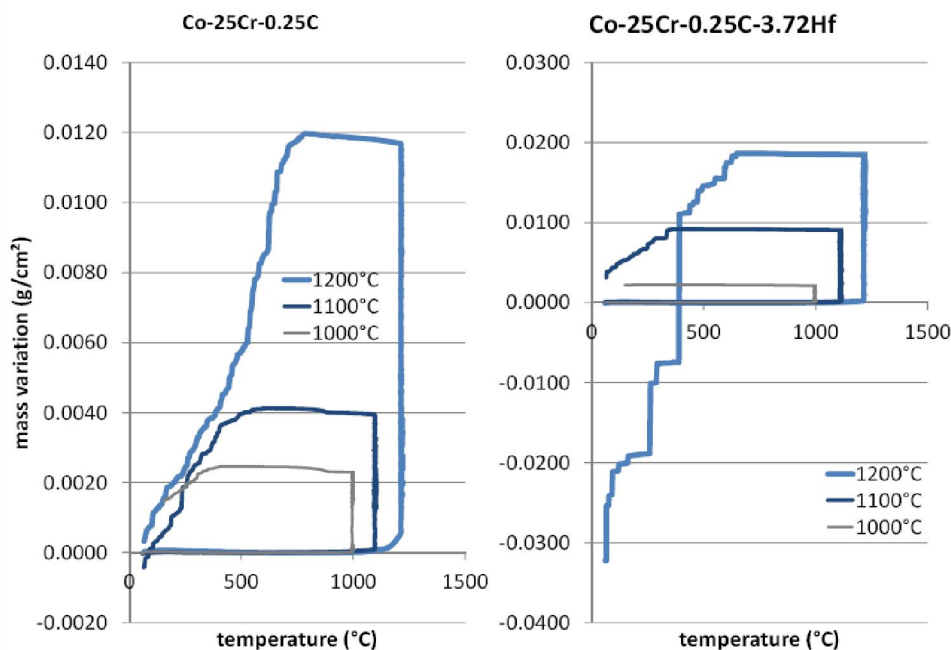

Figure 1 : The whole mass gain curves plotted versus temperature (after correction from the air buoyancy variations[9]) in the case of the two {0.25wt.%C}-containing alloys
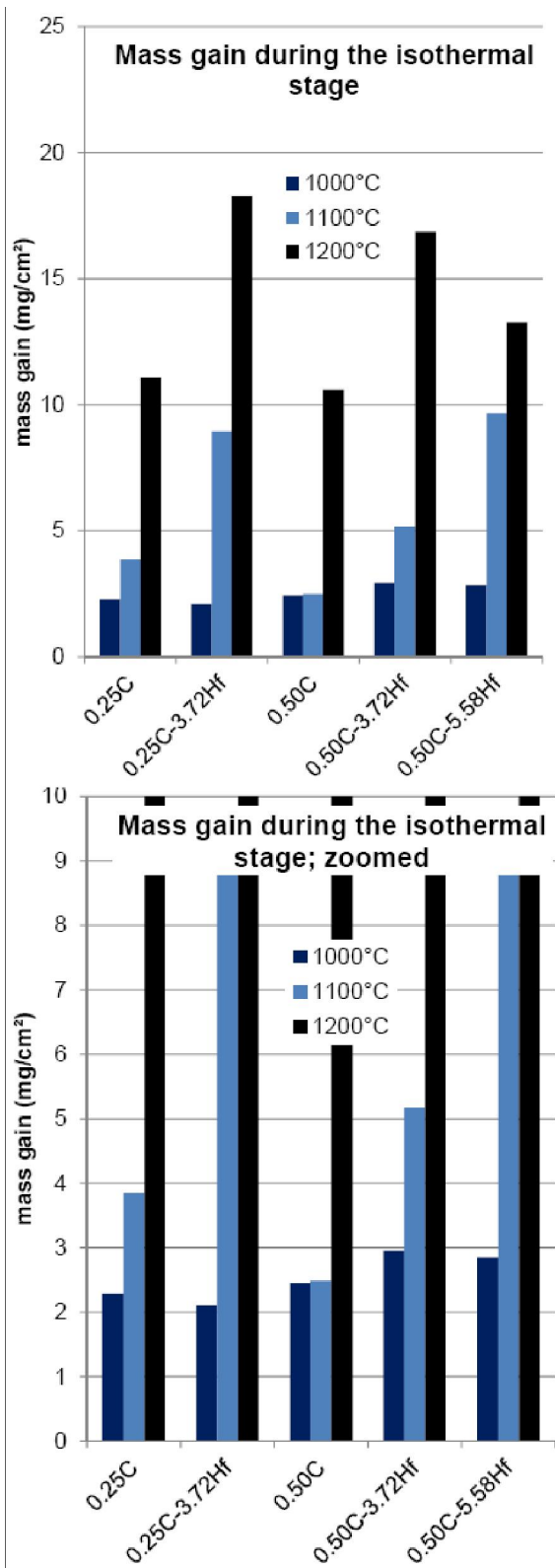
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Figure 3 : Histogram presenting for the five alloys the values of the total mass gain achieved during the isothermal stage (exclusively) realized at either 1000 or 1100°C (this study); the ones previously obtained for 1200°C in an earlier work[9] are also added

temperatures of the {0.25C-3.72Hf}-alloy to the one of the {0.25C}-alloy, and the one of the {0.50C-7.44Hf}-alloy to the one of the {0.50C}-alloy. In contrast the results were seemingly the same for the {0.50C}-alloy and for the {0.50C-3.72Hf}-alloy. This is globally the same effect of the presence of these several weight percents of hafnium that was earlier observed for 1200°C[9]. The effect of Hf is much more important for the cooling from 1000°C as isothermal stage temperature since no oxide spallation were noticed for the three Hf-rich alloys while spallation occurred for the two ternary alloys.

The final mass variations recorded at the return to room temperature are presented in Figure 5. Except for the 1000°C isothermal stage temperature for which oxide spallation occurred only in absence of hafnium in alloy and thus for which the final mass gains are higher for the Hf-rich higher than for the Hf-free ones, it is difficult to see a clear evolution of this second parameter characterizing spallation for the cooling from 1100 and 1200°C. Indeed, this depends, not only on the
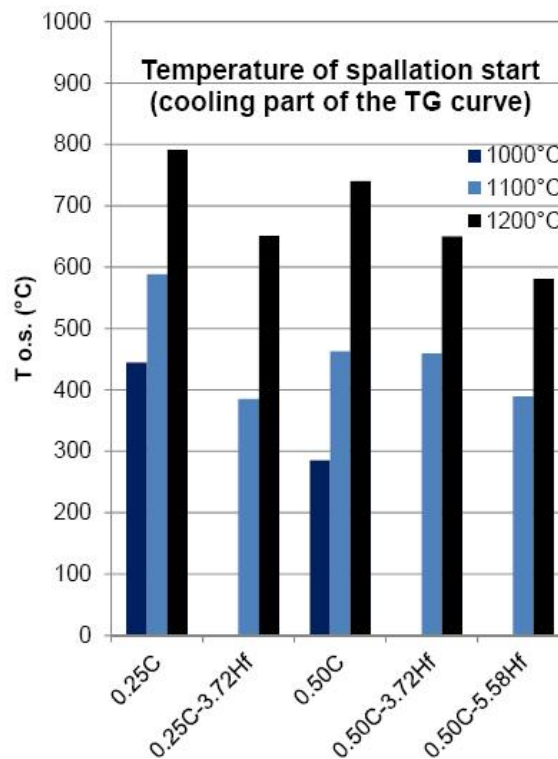

Figure 4 : Histogram presenting the values of the temperature of spallation start during the cooling, for the five alloys, after isothermal stage realized at 1000 or 1100°C (this study), and also at 1200°C (previous study[9]); spallation for only the four first alloys after isothermal oxidation at 1200°C
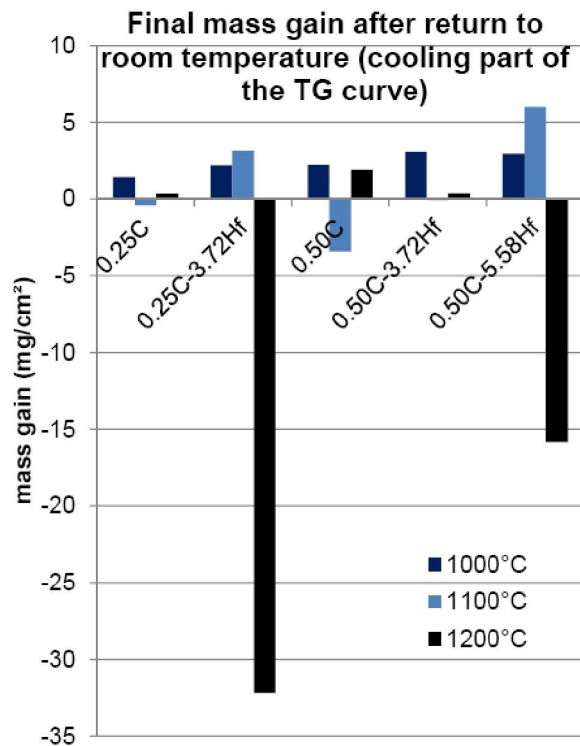
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Figure 5 : Histogram presenting the values of final mass gain at the end of cooling, for the five alloys after isothermal oxidation at 1000 or 1100°C (this study), and also at 1200°C (previous study[9])

occurrence of spallation and on its severity, but also on the value of the mass gain during isothermal oxidation: the higher the isothermal mass gain, the more severe the mass loss if spallation occurs.

After return to room temperature the oxidized sur-

faces of the samples were scanned using a simple office scanner. The obtained images are presented in Figure 6. One can see that the three Hf-containing alloys are still all around covered by the external oxide scales, which is not the case for 1100°C or for the ternary alloys for both temperatures.

General commentaries

Contrarily to what was found in the first part of this work (in which it was rather difficult to deduce relationships between the chemical composition of the alloys and the characteristics of oxidation during heating), the effects of hafnium on the isothermal oxidation kinetic as well as on the parameters characterizing the oxide spallation during cooling were much more obvious. Hafnium appeared here, for these cobalt-based alloys, in the same time as a deleterious element for what concerns isothermal oxidation and as a gainful element for what concerns the resistance of the oxidized alloys against spallation at cooling. It is generally well-known that hafnium is an element favorable for a low oxidation rate, for all types of alloys working at high temperature in oxidant atmospheres, and for cobalt-based alloys in particular. But this seems being true only for Hf contents in alloy not too high. Here, with hafnium contents of several weight percents, the opposite effect was found, as demonstrated by the significantly higher mass gain rates observed for the Hf-rich cobalt alloys by comparison with the corresponding ternary Hf-free
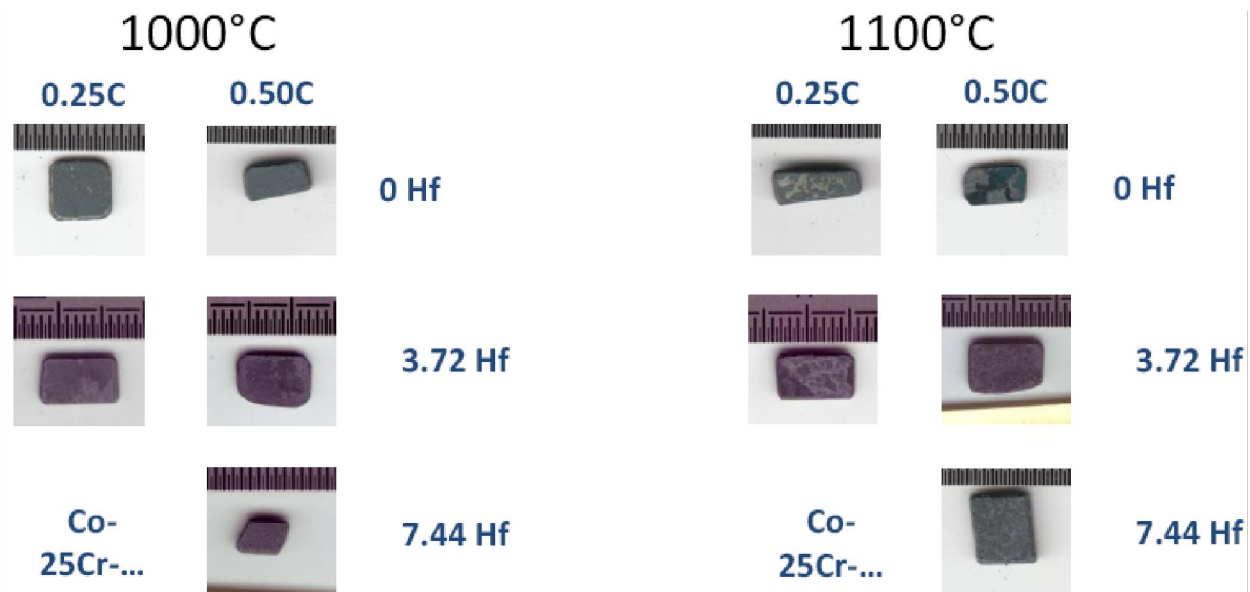

Figure 6 : Surface aspects of the oxidized samples after cooling down to room temperature from 1000 or 1100°C (temperatures of isothermal oxidation); images issued from scanning using an office scanner

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alloys. Otherwise, the presence of hafnium, even with these particularly high quantities, led to a better resistance against spallation of the protective oxide scales. One can here too define a critical Hf content which is comprised between the usual 1 or 2 wt.% Hf content and the present around 4 wt.% Hf content, under which Hf is beneficial for a low oxidation rate and beyond what it is detrimental in contrast. For the nickel-based alloys the critical Hf content defined according to this point of view was higher (between 4 and 6 wt.%Hf)[12]. The results obtained for the iron-based alloys were more scattered (4 to 5 wt.%Hf were beneficial for 1100°C and harmful for 1000 and 1200°C)[13]. Concerning the effect of several weight percents Hf on the scale adherence, the results obtained here for cobalt-based alloys meet the effects seen for the nickel-based and iron-based alloys[12,13].

CONCLUSIONS

Thus, the presence of high hafnium quantities introduced in these cobalt-based alloys did not really deteriorate the high temperature oxidation behavior of these alloys by comparison to Hf-free alloys of the same chemical composition for the other elements. The oxidation rate was more or less accelerated in isothermal conditions but simultaneously the adherence of the formed external oxide scales was improved, which is also important. Similarities of effect of so high hafnium contents were then found between the present cobalt-based alloys and the previously studied iron-based and nickel-based alloys. Thus, transversely, one can add hafnium to chromium-rich alloys in order to strengthen them against high temperature mechanical solicitations, without serious additional risks of high temperature oxidation resistance loss.

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