Effect of a high hafnium content on the high temperature oxidation of chromium-rich cast alloys. Part 4: Isothermal oxidation and scale spallation of Ni-based alloys

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ABSTRACT

The chromium-rich nickel-based alloys without hafnium or with high contents in Hf, previously studied in oxidation during their heating up to 1000°C and 1100°C, were here first characterized in 46 hours-long isothermal oxidation at these temperatures. Second, the cooling parts of the thermogravimetry curves were also exploited, to specify their resistance against oxide spallation. The total mass gains achieved during the isothermal stages were logically higher for a higher temperature, and slightly lower in presence of hafnium for less than 5wt.% of this element. Beyond this limit the oxidation rate may become higher than in absence of hafnium. Concerning the resistance against oxide spallation during cooling the beneficial effect of hafnium, well known for much lower Hf contents, still exists with the Hf contents considered in this work. Chromium-rich nickel-based alloys containing so high Hf contents, for example destined to reinforcement by HfC carbides, still present good behaviour in oxidation at high temperatures, with additionally improvement for notably oxide scale spallation.
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INTRODUCTION

Added to high temperature alloys and superalloys belonging to all families (Co-based, FeNi-based…) to improve their high behaviour in oxidation at high temperature[1], hafnium can be notably found in nickel-based alloys, in bulk materials[2-4] as well as bond coat or coatings[5-8]. The most commonly evocated effects of hafnium are a decrease on oxidation rate and the improvement of the adherence of the external protective oxide scales covering the alloys during thermal cycling for example.

Hafnium is generally added in rather small quantities (typically 1 wt.%) but it can be interesting to investigate its influence when it is present in higher quantities.

Nickel alloys rich in chromium and containing exceptionally high amounts of hafnium (about 4 wt.% and more) were previously elaborated to study the as-cast microstructures which may be obtained in presence of carbon (with a special look to the characteristics of the obtained carbides)[9]. Thereafter the behaviour of these alloys were studied in oxidation at high temperature at 1200°C[10,11]. Since it is also interesting to analyse the

oxidation of such alloys at lower temperatures, the availability of these alloys allowed their characterization in oxidation at 1100 and 1000°C. In a recent work thermogravimetry tests with isothermal stages at these last temperatures were realized and the oxidation behaviour of these alloys during heating analysed[12]. In the present work this are the isothermal oxidation at 1000 and 1100°C and the oxide scale adherence which will be characterized.

EXPERIMENTAL DETAILS

The alloys of the study

One can remind that the nickel-based alloys contain a chromium content (25wt.%Cr for all of them, targeted values) high enough to favour a chromia-forming behaviour and two types of carbon contents (0.25 and 0.50wt.%, targeted values). Three alloys were wished with two levels of hafnium (3.72 and 5.58wt.%Hf, targeted values) and two alloys do not contain Hf (alloys added for comparison). All alloys were earlier prepared by foundry from pure elements[9]. The results previously obtained concerning their oxidation behaviour at 1200°C[10,11] will be included in the present study to enrich the analysis. Names and real chemical composition (measured by Energy Dispersive Spectrometry) are

reminded thereafter:

- "Ni-25Cr-0.25C-3.72Hf": 25.70wt.% Cr and 4.40wt.%Hf (Co: bal., C: not measured)
- "Ni-25Cr-0.50C-3.72Hf": 25.57wt.% Cr and 4.79wt.%Hf (Co: bal., C: not measured)
- "Ni-25Cr-0.50C-5.58Hf": 25.32wt.% Cr and 6.64wt.%Hf (Co: bal., C: not measured)
- "Ni-25Cr-0.25C": 23.79wt.% Cr (Co: bal., C: not measured)
- "Ni-25Cr-0.50C": 22.74wt.% Cr (Co: bal., C: not measured)

A short description of the as-cast microstructures of these alloys was already given in the first part of this work[13]: an austenitic nickel-chromium solid solution matrix and carbides of two types in the interdendritic spaces: 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

The parallelepiped samples used in the thermogravimetry tests, cut in the centre of ingots elaborated by high frequency induction melting in inert atmosphere, were ground with 1200-grade SiC paper (the six faces and the edges and corners). The oxidation tests were performed with a Setaram TG92 thermo-
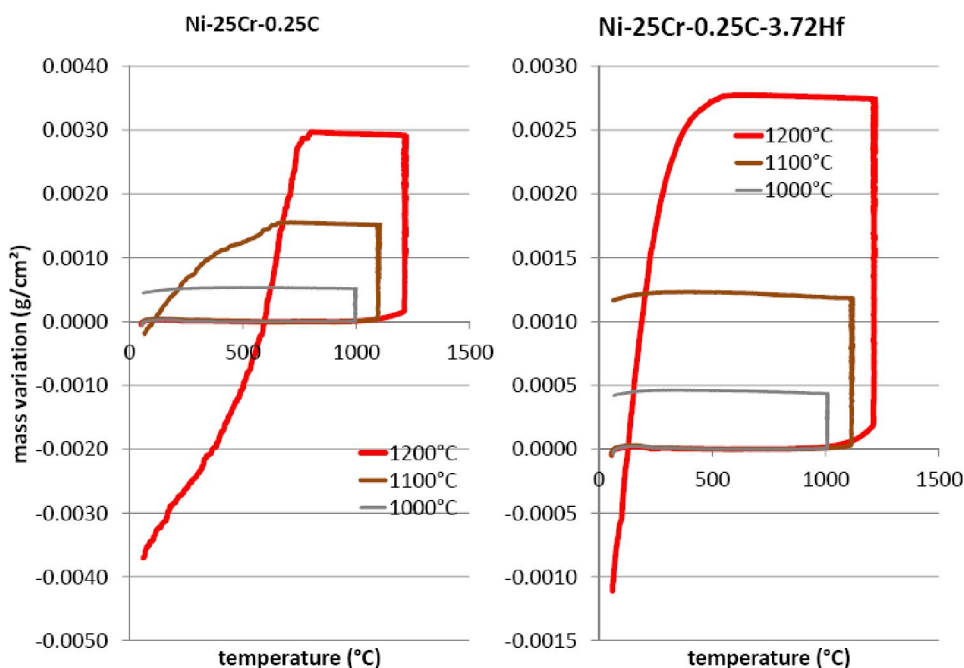

Figure 1 : The whole mass gain curves plotted versus temperature (after correction from the air buoyancy variations[10]) in the case of the two {0.25wt.%C}-containing alloys
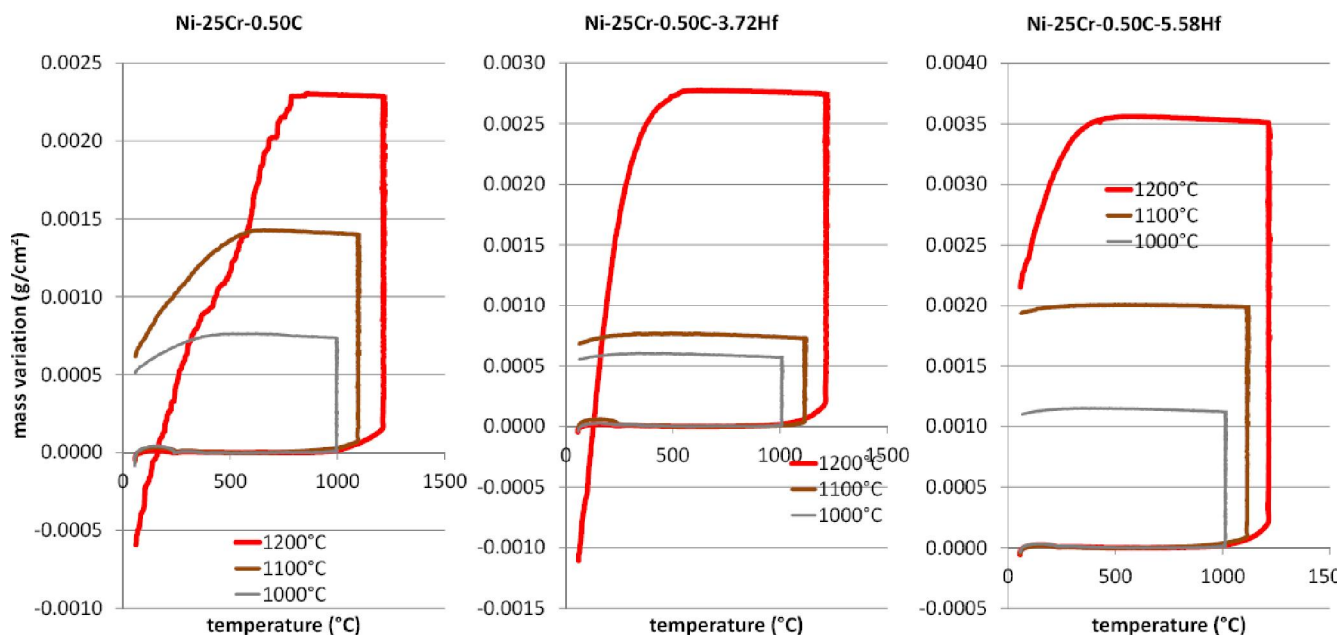
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Figure 2 : The whole mass gain curves plotted versus temperature (after correction from the air buoyancy variations[10]) in the case of the three {0.50wt.%C}-containing alloys

balance in dry synthetic air, following a thermal cycle composed of a heating at 20°C min^{-1}, an isothermal (1000 or 1100°C)-stage during 46 hours, and a cooling at -5°C min^{-1}. The total mass gains resulting from the isothermal oxidation was considered, and cooling parts of the mass gain curves were exploited according to a method earlier presented in previous work[13]: mass gains plotted versus temperature (instead versus time) were corrected from the variations of air buoyancy, and the cooling parts of the obtained new curves led to:

- the temperature at which the curve becomes irregular during cooling because of oxide spallation (oxide spallation start temperature)
- the final mass variation (which depends on the global oxidation kinetic and on the severity of the oxide spallation)

RESULTS AND DISCUSSION

The {mass gain versus temperature}-curves: isothermal part and cooling part

The whole curves (plotted versus temperature after correction from the air buoyancy variations) obtained for the two {0.25wt.%C}-containing alloys for the three temperatures are displayed in Figure 1. What can be globally seen is that the isothermal mass gain logically

increases with temperature and that the Hf-containing alloy oxidized significantly slower than the Hf-free one, this at each of the three temperatures.

Concerning the behaviour of the external scale during the cooling, one can see that the isothermally oxidized at 1000°C Hf-free alloy did not lose parts of its external oxide during the cooling down to ambient temperature. In contrast spallation appears on the 1100°C-curve and it was previously seen that it was especially severe after isothermal oxidation at 1200°C (negative mass gain after return to room temperature). For the Hf-containing alloy spallation did not occurred during cooling after isothermal oxidation at 1100°C. After isothermal oxidation at 1200°C, one can remind that continuous spallation took place but with a not so high mass loss at the end (after return to room temperature).

The whole curves (plotted versus temperature after correction from the air buoyancy variations again) obtained for the three {0.50wt.%C}-containing alloys for the three temperatures are displayed in Figure 2. In the three graphs one can see again that the higher the 46 hours-isothermal oxidation temperature, the higher the achieved mass gain. By observing the cooling parts of the curves one can see that the Hf-free alloy knew rather continuous oxide spallation during the cooling after the 1100°C stage while the oxide loss is more severe (negative final mass variation) and irregular during the
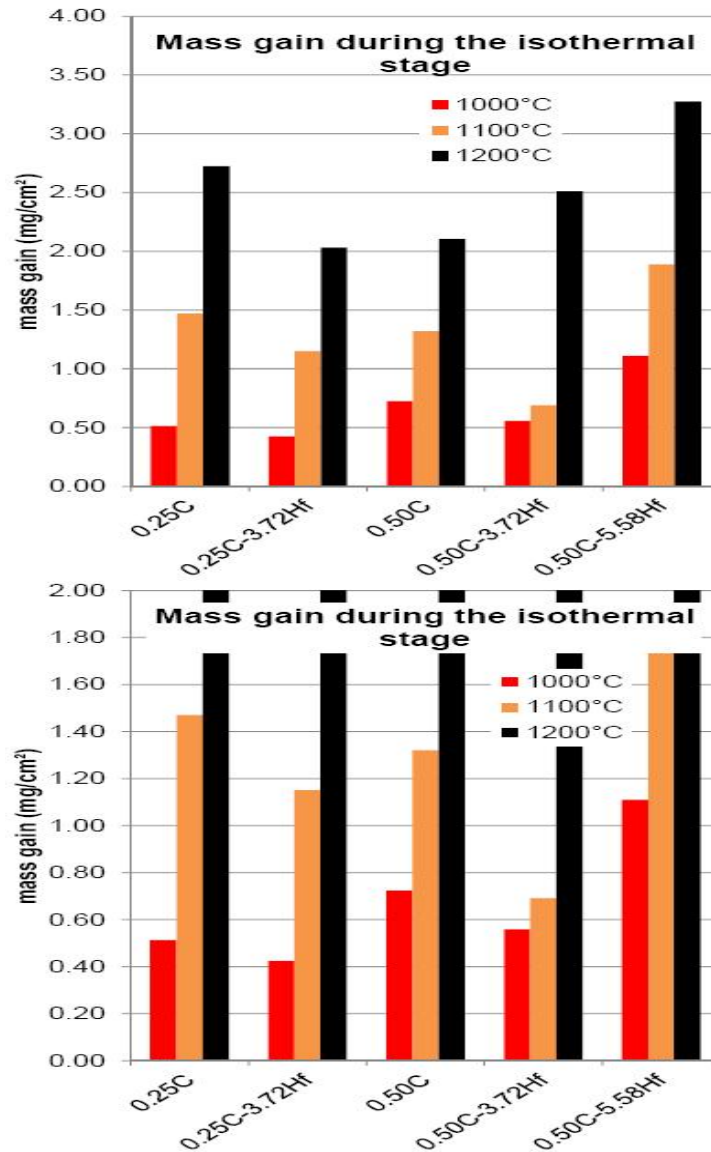
Figure 3 : Histogram presenting for the five alloys the values of the total mass gain achieved during the isothermal stage (exclusively) realized at either 1000 or 1100°C (this study); the ones previously obtained for 1200°C in an earlier work[10] are also added

cooling after the 1200°C stage. The {0.50C-3.72Hf}-containing alloy was not affected by oxide spallation during cooling neither from the 1000°C stage nor from the 1100°C stage. During the cooling from 1200°C it seems that oxide spallation happened but very continuously. However the final mass variation was negative. No spallation occurred during the cooling from 1000°C and during the cooling from 1100°C for the {0.50C-5.58Hf}-containing alloy. A continuous oxide loss seems having taken place during the cooling from 1200°C but, in contrast with the {0.50C-3.72Hf}-containing alloy, the mass gain was still positive after return to room tem-

perature.

The comments made above qualitatively about the isothermal oxidation are confirmed by seeing this time the quantitative data presented in Figure 3. In the top histogram, and especially in the enlarged view given in the bottom histogram, it appears clearly that the addition of hafnium decreases the isothermal mass gain for all alloys at 1000 and 1100°C. At 1200°C this was not so clear[10] since this was the contrary which was observed for the 0.50C-alloys. However the fast increase in isothermal mass gain for 1000°C and 1100°C if the Hf content is particularly high ({0.50C-5.58Hf}-con-
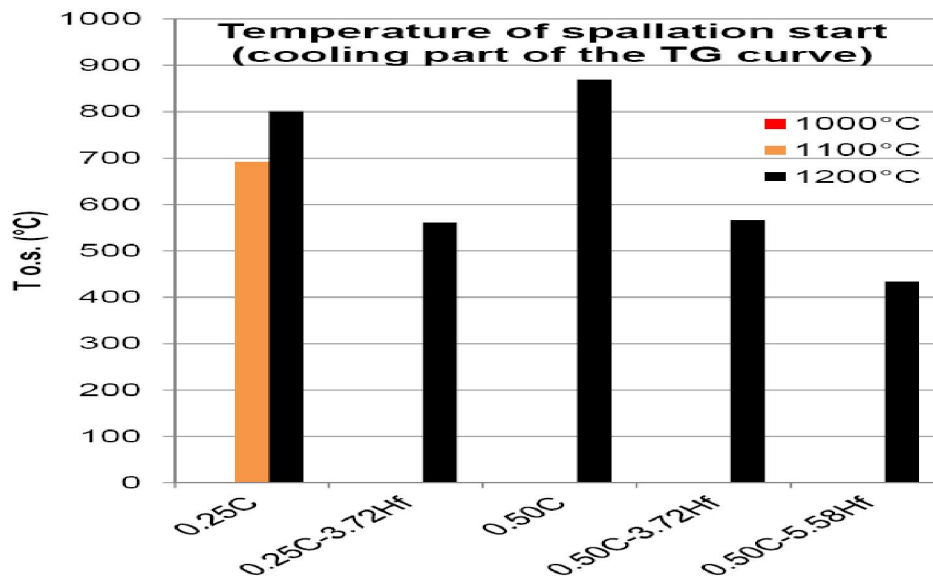
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Figure 4 : Histogram presenting the values of the temperature of spallation start during the cooling, for the five alloys, after isothermal stage realized at 1000 or 1100°C (this study), and also at 1200°C (previous study[10]); spallation for only the four first alloys after isothermal oxidation at 1200°C
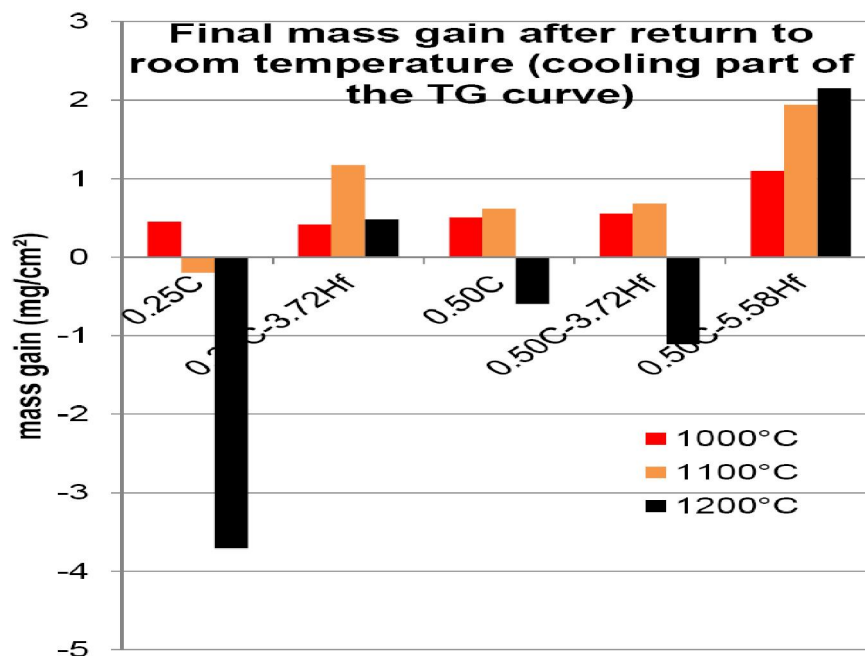

Figure 5 : Histogram presenting the values of final mass gain at the end of cooling, for the five alloys after isothermal oxidation at 1000 or 1100°C (this study), and also at 1200°C (previous study[10])

taining alloy}, was also found earlier for 1200°C[10].

Oxide spallation at cooling

The behaviour of the alloys concerning the oxide spallation during the cooling after the isothermal stage can be shortly described by three criteria: existence of spallation or not, in case of spallation temperature at which it occurred, and final mass of the oxidized sample after return to room temperature (measured in the

thermo-balance since additional oxide loss may happen during the manipulation of the oxidized sample outside).

Oxide spallation during cooling occurred only during the cooling from 1200°C for all alloys, and also during the cooling from the 1100°C-stage for the Ni-25Cr-0.25C alloy. For this latter alloy, it is visible in Figure 4 that the temperature at which a mass loss which
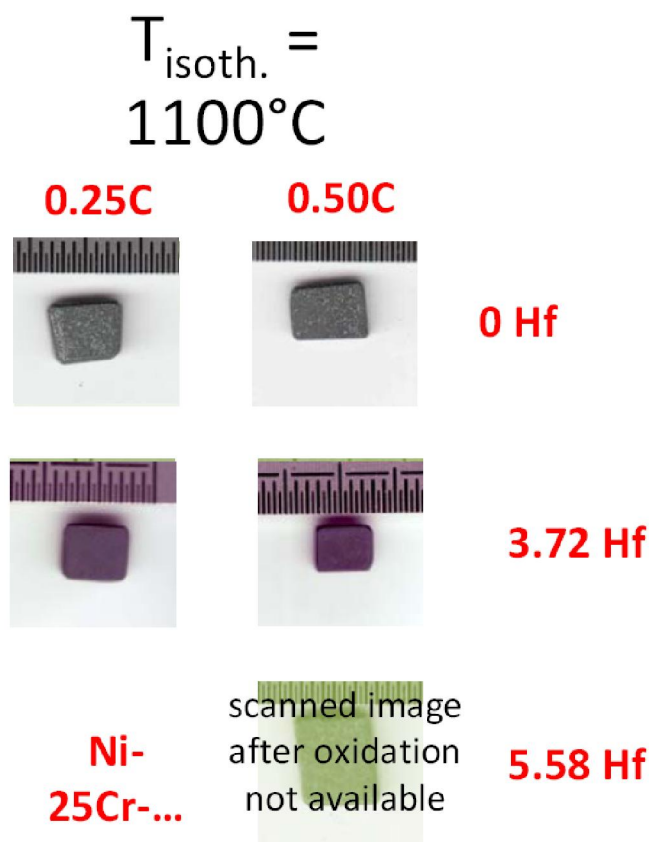
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Figure 6 : Surface aspects of the oxidized samples after cooling down to room temperature from 1000 or 1100°C (temperatures of isothermal oxidation); images issued from scanning using an office scanner

can be attributed to oxide spallation was detected, is lower for the cooling from the 1100°C-stage than for the cooling from the 1200°C-stage. For all alloys, for the cooling from the 1200°C-stage during which spallation occurred, it clearly appeared[10] that the presence of hafnium, and if effectively present a higher hafnium content, delayed the spallation start to lower temperatures. Indeed the spallation start temperature was lower for the 0.25C-3.72Hf alloy than for the 0.25C one, and lower for the for the 0.50C-3.72Hf alloy than for the 0.50C one. In addition, increasing again the Hf content for 0.50C-alloy diminished again the oxide spallation temperature.

The final mass gains after return to ambient is graphically presented in Figure 5, with again the presence of the results for the 1200°C-stage tests[10]. At 1200°C the residual mass gains were generally higher with the presence of hafnium and with its content. For 1000 and 1100°C this is systematically true.

The oxidized states of the five alloys after 46 hours

– oxidation at 1000 or 1100°C and cooling to ambient temperature are illustrated in Figure 6 by images issued from scanning. The samples seem to be all wholly covered by the external oxide. However, the two samples having shown irregular cooling parts and low or negative final mass gains (the two Hf-free alloys cooled from the 1100°C-stage) have here and there lost small particles of external oxide with consequently local appearance of the metallic substrate.

General commentaries

The exploitation of the final 1000°C- and 1100°C-isothermal oxidation mass gains and of the cooling parts of the thermogravimetry curves were thus very useful to characterize the effect of the presence of hafnium in nickel-based alloys in so high proportions. First the mass gains at the end of the isothermal stages were clearly decreased by the presence of hafnium, except in the case of the {050C-5.58Hf}-alloy which was probably too rich in this elements (real content 6.64wt.% measured by EDS). It is possible that in this alloy's family it exists a limit Hf content between 5 and 6 wt.% (real content) beyond which Hf is too much exposed to oxidation and bring a significant contribution to the mass gain. Always for this alloy's family the Hf contents were never too high to possibly inverse the beneficial effect on the adherence of the oxide scale during the cooling. There is seemingly no such limit for the Hf content below 7wt.%Hf for this second property.

CONCLUSIONS

After having previously seen that such high Hf contents may sometimes lead to sooner oxidation start during heating and to higher total mass gains when reaching the isothermal stage beginning, one saw here that the isothermal oxidation may be also a little accelerated but only for the highest Hf content tested here. Indeed the beneficial effect of this element generally observed for much lower Hf contents still exists for less than 5wt.%Hf (real content). Despite that one can initially fear that so high Hf contents may deteriorate the general high temperature oxidation behavior of these alloys Hf does not threaten their resistance against this phenomenon. On the contrary the resistance against oxide spallation during cooling (and then probably during ther-

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mal cycling) is still improved by comparison with equivalent Hf-free alloys. Hf can be thus seemingly present in alloys with very high contents, for example to develop significant HfC network for high temperature mechanical resistance purpose, without bad consequences for the resistance to oxidation at high temperature of these nickel alloys and for other similar alloys chromium-rich nickel-based alloys.

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