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# Elaboration and Metallographic Study of {M-25Cr}-based Alloys Containing Hafnium Carbides (M=Co, Ni or Fe): Microstructures in the As-cast State and after Exposure at 1200°C

Patrice Berthod\* and Elodie Conrath

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## Abstract

Six chromium-rich M-based alloys (M=Co, Ni or Fe) with conventional carbon contents (0.25 and 0.50wt.%) and containing near 4wt.% of hafnium were elaborated in foundry. As expected, dense precipitation of hafnium carbides was achieved, with repartitions and shapes similar to what it is generally obtained with tantalum carbides. Chromium carbides were also obtained in some alloys. After exposure of samples at 1200°C for about 48 hours the HfC carbides network was kept without significant changes of morphology and surface fractions, in the cobalt-based and nickel-based alloys, in contrast with the iron alloys which appeared less stable. Indentation performed in as-cast and aged samples showed that these HfC-containing alloys display various hardness values. The HfC-containing cobalt alloys are the hardest ones and the high temperature exposure induced a limited lowering of this property. The cast HfC-containing cobalt alloys are potentially very interesting for applications at very high temperature requiring foundry equi-axed chromium-rich alloys.

*Keywords:* Cobalt-based alloys; Nickel-based alloys; Iron-based alloys; HfC carbides; Hafnium carbides; High temperature microstructure

## 1. Introduction

Nowadays the best refractory metallic materials for applications at very high temperature are the  $\gamma/\gamma'$  single crystal superalloys (Donachie and Donachie, 2002). These nickel-based superalloys contain high quantities in aluminum, necessary to the gamma prime precipitation and additionally allowing them displaying an alumina-forming behavior (Kofstad, 1988). Chromium is another element which can be also added to superalloys to resist oxidation by hot gases. Despite that this

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second element is slightly less efficient than aluminum, chromium is almost compulsory when the alloy must be in contact with aggressive liquid substances (e.g. molten glass for example). Unfortunately aluminum and chromium cannot be simultaneously present in a same superalloy with high quantities for both of them. Consequently chromium-rich superalloys highly resistant against hot corrosion by molten substances cannot be reinforced by gamma prime precipitates. Other reinforcing means exists to resist high temperature stresses and creep deformation (Bradley, 1988; Sims and Hagel, 1972), as solid solution strengthening, nano-oxides dispersion (mainly alloys elaborated by powder metallurgy route), precipitation of secondary carbides obtained by special heat treatment (cast or forged alloys), or by crystallization of interdendritic primary carbides at solidification (cast alloys). This later type of mechanical reinforcement of superalloys especially concerns cobalt-based superalloys which cannot be generally strengthened by gamma prime precipitation. In contrast reinforcement by primary carbides are more rarely employed for nickel-based, {nickel+iron}-based or iron-based refractory alloys.

Chromium carbides are sometimes used to reinforce some cast alloys based on Co, Ni and/or Fe but these carbides are not sufficiently stable at very high temperature (more than 1000°C) during long exposures (more than 100 hours). A first type of MC carbides – TaC – presents a better behavior in these conditions but only in cobalt-based (Berthod et al., 2003), { nickel + iron } - based (Berthod et al., 2007) and iron-based chromium-rich cast alloys (Berthod et al., 2007). Indeed they tend, first to do not appear at solidification, and second to disappear at high temperature, in nickel-based chromium-rich alloys (Berthod et al., 2004). However, at temperatures as high as 1200°C the TaC carbides tend to get fragmented and their volume fraction tends to decrease, with as consequence a decrease in their strengthening potential.

It was fortunately seen in a previous work (Berthod, 2009), in chromium-rich cobalt-based cast alloys, that another type of MC carbides – HfC – seems being more stable at very high temperature than the TaC carbides. As the TaC carbides, during solidification of these cobalt-based alloys, the HfC carbides precipitated in the interdendritic spaces as script-like eutectic carbides mixed with matrix. Thus, hafnium, the best known effect of which is to improve the resistance of superalloys against high temperature oxidation (Ribaudo and Mazumder, 1989) is also an element leading to carbides which seem being able to ensure high mechanical resistance on long times at high temperature.

The HfC carbides were curiously not often considered for the mechanical reinforcement of superalloys at high temperature. There were rather employed in cobalt-based hard metals, directionally solidified nickel-based alloys, molybdenum-based or tungsten-based alloys (Bouhanek et al., 1997; Kim, 1978; Witzke, 1976; Chen et al., 1989), to improve the mechanical properties of these alloys. Considering a reinforcement of cast chromium-rich alloys by HfC carbides appears to be rather new.

In this work six 25wt.%Cr-containing alloys were elaborated, two cobalt-based, two nickel-based and two iron-based alloys, all containing 3.72wt.%Hf (targeted content), a value higher than generally found for this element in conventional superalloys. First it was wished to verify whether the script-like shape and interdendritic repartition of the HfC carbides is found again in the cobalt-based alloys, and to observe whether these carbides also appear in {Ni-25wt.%Cr}-based alloys and in {Fe-25wt.%Cr}-based alloys. Second all these alloys were subjected to long exposure at 1200°C in order to observe how the microstructures of these alloys behave (notably the HfC carbides if

initially present) at a so high temperature, in order to evaluate the sustainability of the potential high temperature mechanical reinforcement that they would bring to the alloys.

## **2. Experimental**

### **Elaboration of the alloys and high temperature tests**

The six alloys studied in this work were targeted with the following chemical compositions:

“M (bal.)-25Cr-0.25C-3.72Hf” (contents in wt.%) with M=Co, Ni or Fe

“M (bal.)-25Cr-0.50C-3.72Hf” (contents in wt.%) with M=Co, Ni or Fe

The choices of the carbon and hafnium contents were done in order to try obtaining exclusively HfC carbides (same atomic contents for carbon and hafnium with 0.25wt.%C and 3.72wt.%Hf) or a mix of HfC carbides and of chromium carbides (by multiplying the C content by 2 for a same Hf content).

These alloys were all elaborated following the same foundry route:

- preparation of the charges with pure elements (Co or Ni or Fe, Cr, Hf, C: Alfa Aesar, purity > 99.9%); about 40g,
- introduction of the metallic elements in the water-cooled copper crucible of a High Frequency induction furnace (operating parameters: frequency of about 110kHz, voltage of about 4000V), isolated from exterior with a silica tube,
- three cycles {primary vacuum – 800 millibars of pure argon}, finished by the final establishment of 300 millibars of argon,
- heating, high temperature (about 1600°C) stage during 5 minutes, cooling and solidification in the furnace in the inert atmosphere of Ar.

The obtained compact-shaped ingots were cut using first a Buelher Delta Abrasimet cutter, and second a Buelher IsoMet 5000 linear precision saw. The obtained parallelepipeds (about  $9 \times 9 \times 4$  mm<sup>3</sup>) were polished with SiC papers with grade up to 1200, with smoothing of edges and corners to avoid possible fast alloy deterioration by hot oxidation during the high temperature exposures. They were all subjected to a 1200°C isothermal dwell during  $48 \pm 2$  hours in a resistive furnace in air.

### **Metallographic characterization and hardness measurements**

An as-cast sample per ingot, as well as the parallelepipeds exposed to 1200°C (the later after post-treatment cutting), were all subjected to metallographic preparation and characterization.

They were thus first embedded in a cold resin mixture (resin CY230 + hardener HY956, ESCIL), then polished with SiC papers with grade from 120 to 1200, cleaned using an ultrasonic device, and then finished with textile disk enriched with 1µm alumina particles.

The metallographic samples prepared from as-cast alloys were subjected to X-Ray Diffraction (XRD) and their chemical compositions determined by Energy Dispersion Spectrometry (EDS). The

as-cast samples and the 1200°C-aged samples were examined using a Scanning Electron Microscope (SEM, JEOL JSM 6010 LA) in Back Scattered Electrons (BSE) mode, at different magnifications. Per sample three {×1000}-BSE micrographs were analyzed using the Photoshop CS software of Adobe to measure the surface fractions of the different carbides present in their microstructures. Pinpoint EDS measurements were performed on the different particles to identify them, and in the matrix to specify its Cr and Hf contents.

The mounted samples (as-cast and aged samples) were also subjected to Vickers indentations. This was performed using a Testwell Wolpert apparatus, under a 30kg-load.

### 3. Results

#### The obtained chemical compositions and as-cast microstructures

The obtained Cr and Hf weight contents assessed by EDS measurements for the six alloys are presented in Table 1 (except carbon which cannot be analyzed by EDS).

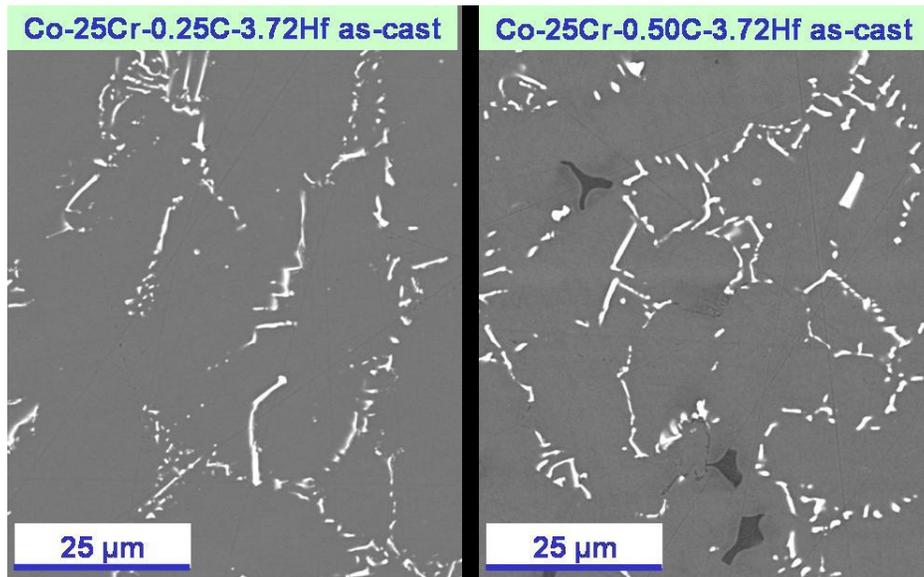
**Table 1** The obtained chemical compositions for the alloys (all contents in weight percents)

Alloy	Cr	Hf
“Co-25Cr-0.25C-3.72Hf” alloy	25.5	3.8
“Co-25Cr-0.50C-3.72Hf” alloy	25.6	3.9
“Ni-25Cr-0.25C-3.72Hf” alloy	25.7	4.4
“Ni-25Cr-0.50C-3.72Hf” alloy	25.6	4.8
“Fe-25Cr-0.25C-3.72Hf” alloy	25.7	3.9
“Fe-25Cr-0.50C-3.72Hf” alloy	25.6	3.5

They globally well respect the targeted contents, notably for chromium.

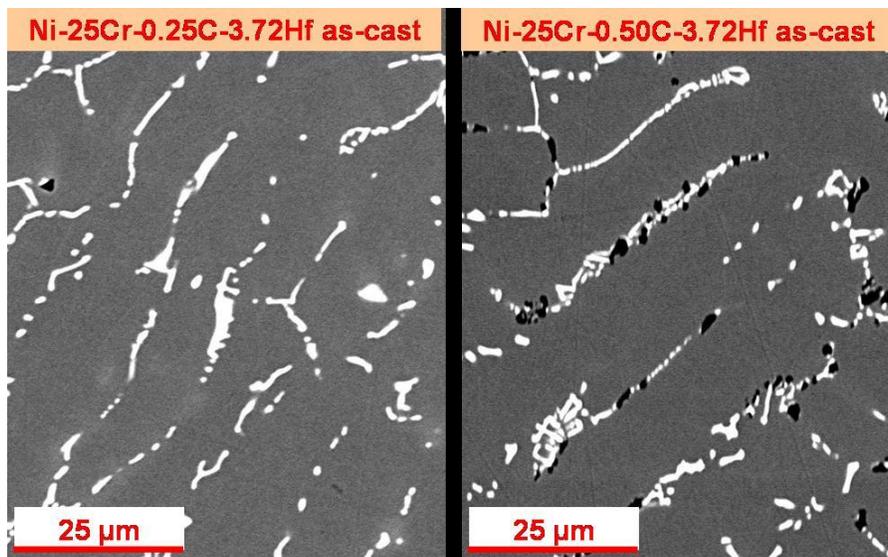
The as-cast microstructures of the two cobalt-based alloys, the two nickel-based alloys and the two iron-based alloys are illustrated by SEM/BSE micrographs in Fig 1., Fig 2., and Fig 3., respectively.

The 0.25C-containing Co-based alloy is composed of a dendritic matrix of cobalt solid solution and of carbides appearing in white in BSE mode (Fig 1.). The microstructure of the 0.50C-containing Co-based alloy is similar but there are seemingly more carbides in this second alloy. Some of them are black. The XRD runs show that the matrixes of the alloys are double-phased, with the presence of the high temperature austenitic form and the low temperature hexagonal one. The obtained diffractograms also show that HfC carbides are probably present but the peaks are both rather small and partially mixed with the peaks corresponding to the two forms of matrix. In contrast the chromium carbides, with surface fractions lower than for the HfC carbides, were not detected by XRD and therefore not identified. However EDS pinpoint measurements clearly showed that Hf was present in very high concentrations in the white particles, that Cr was also present with high concentrations in the dark particles, and qualitatively that carbon is also present in the two types of particles. This demonstrates that the white particles, present in the two alloys, are HfC carbides and the dark particles, present only in the second alloy, are chromium carbides. Concerning the later ones, too rare to be detected by XRD and too small to allow an accurate chemical composition determination (notably for the too light C element), no information about their stoichiometry was obtainable.



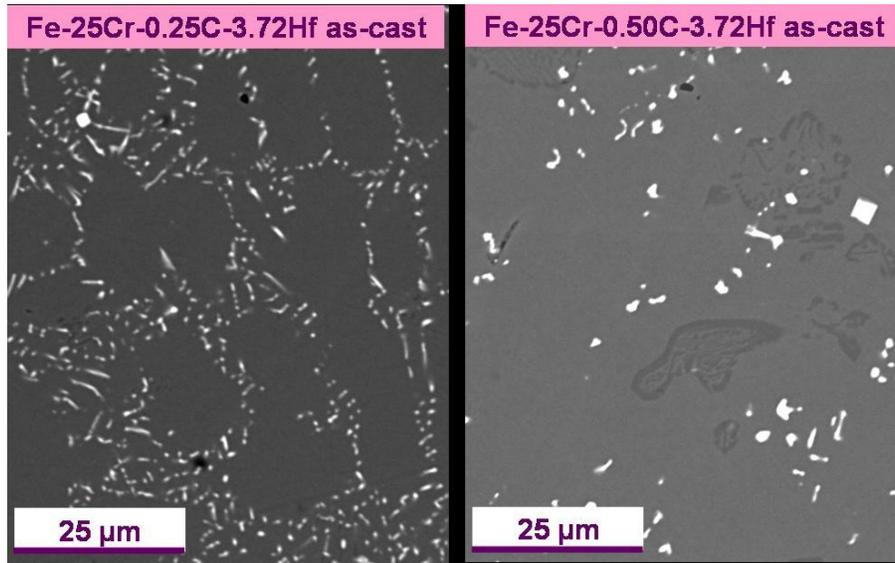
**Fig 1.** As-cast microstructures of the two Hf-containing cobalt alloys

The microstructures of the two nickel-based alloys are showed in Fig 2. Similarly to the cobalt-based alloys, the two alloys based on nickel are composed of a dendritic matrix and of white particles, with additionally rarer black particles in the 0.50C-containing alloy. The matrix is logically austenitic, as confirmed by X-Ray Diffraction. These same techniques also showed that there are also HfC carbides (the white particles), as qualitatively confirmed by another way (pinpoint EDS measurements). The black particles, too rare to provide peaks with XRD experiments, seems being chromium carbides, as suggested by the high concentrations in chromium revealed by EDS, and seemingly the ones in carbon too.



**Fig 2.** As-cast microstructures of the two Hf-containing nickel alloys

The iron-based alloys are a little different. Their microstructures, presented in Fig 3., show too an interdendritic network of white HfC carbides, with the presence of dark chromium carbides even in the 0.25C-containing alloy. The HfC carbides are obviously fragmented by comparison with the four preceding alloys based on cobalt or on nickel. The chromium carbides, which are already present in the low carbon iron alloy, exist in significant fraction in the high carbon iron alloy. They obviously form a eutectic compound with matrix.



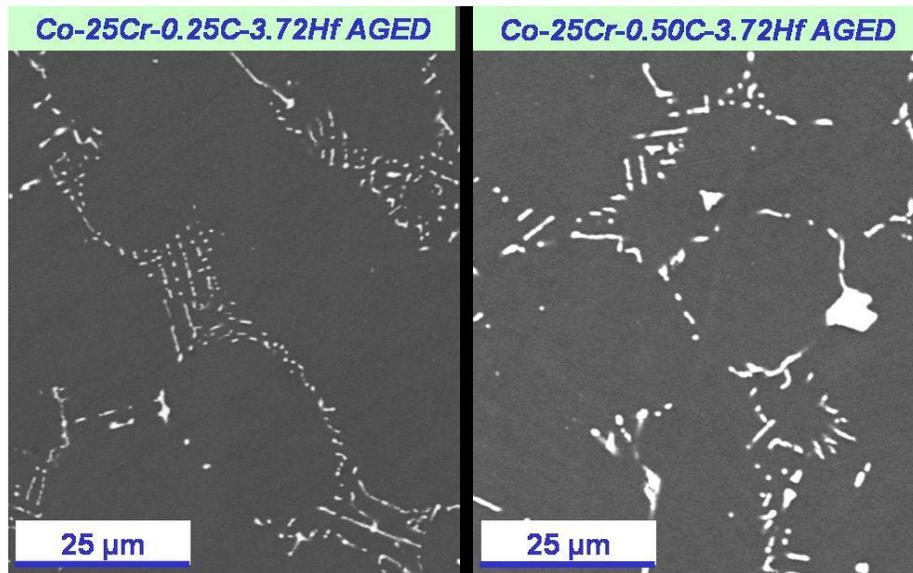
**Fig 3.** As-cast microstructures of the two Hf-containing iron alloys

### Microstructures after high temperature exposures

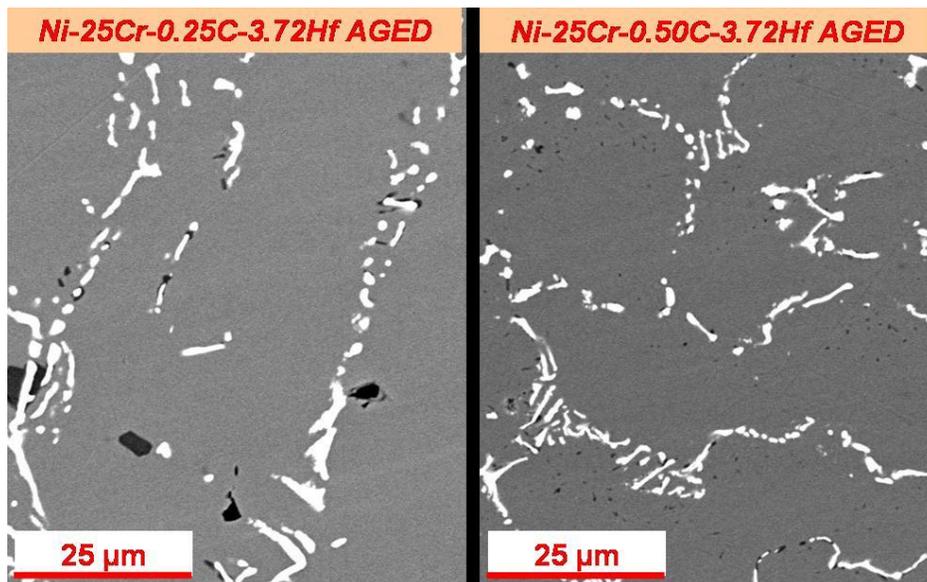
The microstructures of the alloys have more or less evolved during the exposures at 1200°C. The differences are rather small limited for the cobalt-based alloys (Fig 4.) since one can notice here and there a very limited fragmentation of the script-like HfC carbides in both alloys, as well as a decrease in chromium carbides quantity in the high carbon cobalt alloy. HfC fragmentation also occurred a little in the two nickel-based alloys (Fig 5.). In addition chromium carbides obviously precipitated even in the low carbon nickel alloy. Fragmentation was more severe for the HfC carbides of the two iron alloys (Fig 6.). Their chromium carbides have simultaneously coarsened, notably in the high carbon iron alloy.

In addition to morphology, the surface fractions of the two types of carbides were also studied. Per sample three { $\times 1000$ }-BSE micrographs were subjected to image analysis. This led to the results graphically represented in Fig 7. for the hafnium carbides, and in Fig 8. for the chromium carbides. One can see that the surface fraction of HfC was similar for all alloys in the as-cast state (about 4.5 surf.%), except for the high carbon iron alloy (only 2 surf.%). The surface fractions of chromium carbides are not significant in the low carbon alloys, whatever the base element. In the high carbon alloys it increases between the cobalt alloy (about 0.6 surf.%) and the nickel one (about 2.6 surf.%). The iron alloy is the richest one in chromium carbides (about 3.6 surf.%).

After exposure at 1200°C the HfC surface fractions have slightly decreased for the two cobalt alloys and for the two nickel alloys while, in contrast, it has increased a little in the low carbon iron alloy and much more in the high carbon one. In the same time all chromium carbides have disappeared in the two cobalt alloys which now both contain HfC carbides only. Chromium carbides are more present in the 0.25C-containing nickel (1.7 surf.%) and iron (2.0 surf.%) alloys. Inversely their surface fraction has decreased in all the 0.50C-containing alloys.



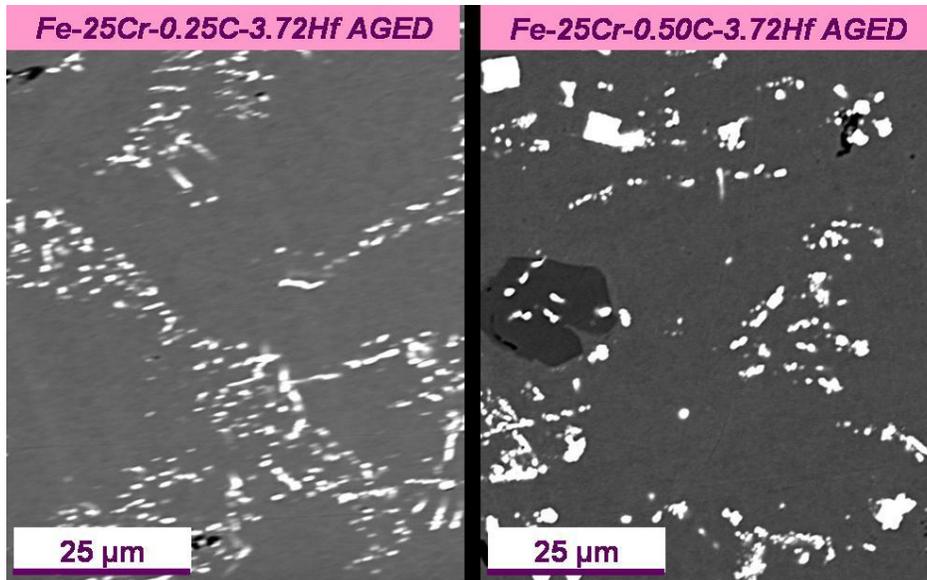
**Fig 4.** Aged microstructures of the two Hf-containing cobalt alloys



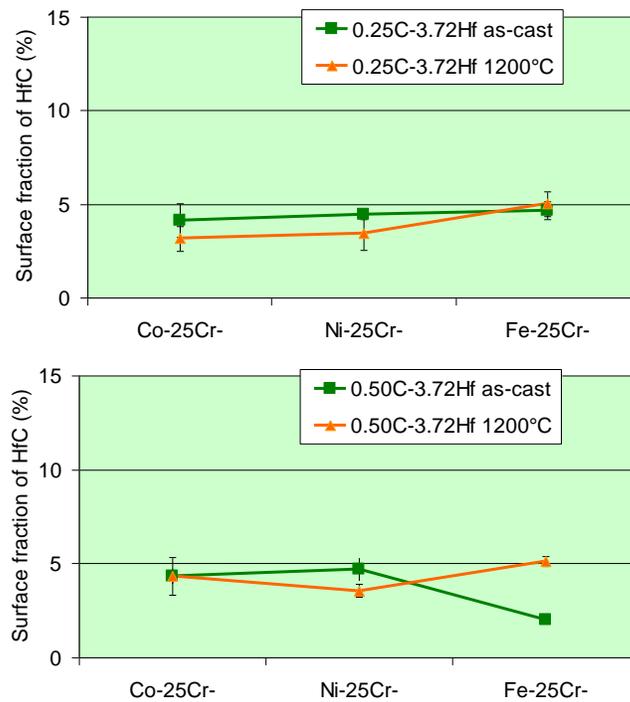
**Fig 5.** Aged microstructures of the two Hf-containing nickel alloys

The as-cast samples and 1200°C-aged samples were subjected to Vickers indentation with a load of 30kg. For each sample an average value and a standard deviation value were calculated from three

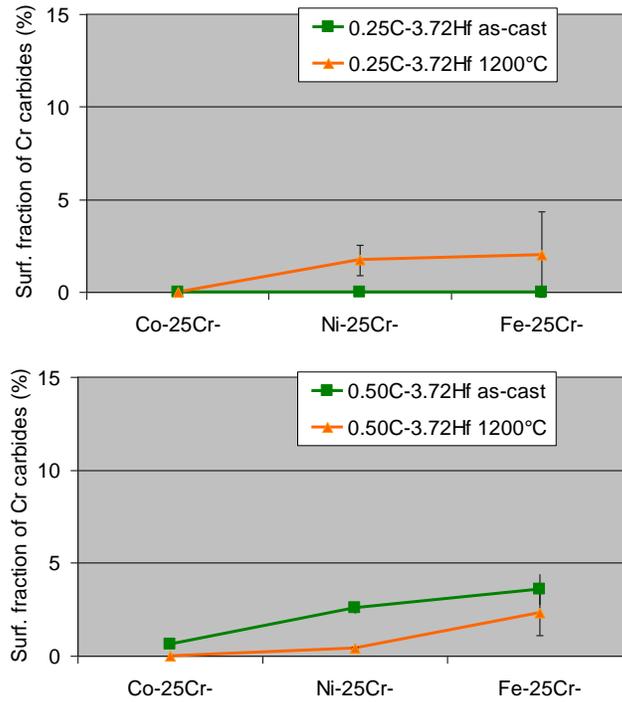
measures. The results are graphically presented in Fig 9.



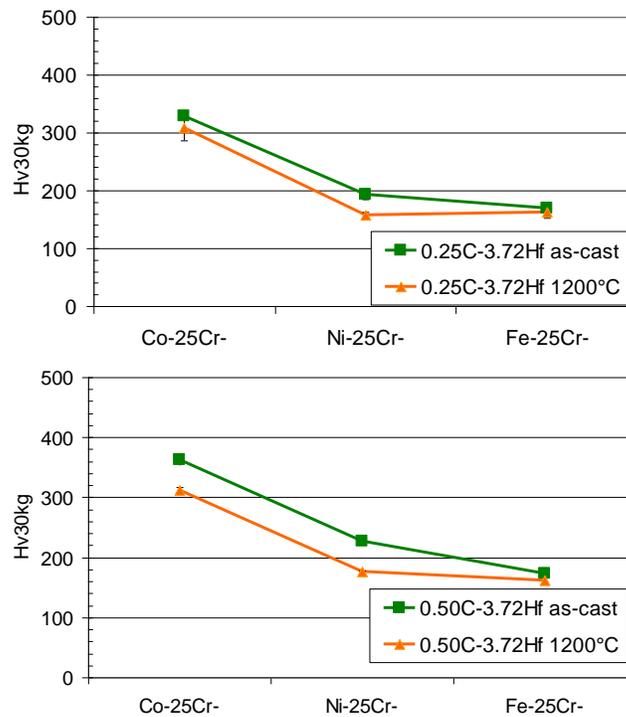
**Fig 6.** Aged microstructures of the two Hf-containing iron alloys



**Fig 7.** Surface fractions of the HfC carbides in all alloys in their as-cast and aged states



**Fig 8.** Surface fractions of the chromium carbides in all alloys in their as-cast and aged states



**Fig 9.** Average hardness of all alloys in their as-cast and aged states

### **Hardness in the as-cast state and in the aged state**

In the as-cast state the cobalt-based alloys (330-360) are harder than the nickel-based ones (195-225), while the later ones are themselves slightly harder than the iron-based alloys (both around 170). In each family the hardness is logically higher for the 0.50C-containing alloy than for the 0.25C-containing one, except for the iron alloys, the hardness average values of which are very close to one another. After exposure to 1200°C the hardness has decreased in all cases, but more for the cobalt alloys (both around 310) and the nickel alloys (both around 165) than for the iron ones (both around 162).

## **4. Discussion**

By considering a carbon range typical of most of commercial chromium-rich carbides-strengthened superalloys and by introducing hafnium in quantities high enough, dense precipitations of HfC carbides were successfully obtained. This was known for cobalt alloys (Berthod, 2009) but not for nickel alloys and iron alloys. In the case of the [0.25C, 3.72Hf] combination – weight contents (corresponding to the atomic equivalence between the two elements) an interdendritic network of script-like HfC carbides forming an eutectic with matrix was obtained in the three systems (base Co, Ni and Fe). Hafnium showed thus a predominant carbide-forming behavior by comparison to the other carbide-former element present: chromium. This is not necessarily the case for all the other MC-forming elements since, for example, chromium carbides earlier demonstrated a high stability than the TaC carbides in nickel-based alloys (Berthod et al., 2004). TaC were in contrast more stable than chromium carbides in cobalt-based (Berthod et al., 2003) and iron-based alloys (Berthod et al., 2007). In the 0.50C-containing alloys the carbon atoms, which are in excess with respect to the hafnium atoms, led to chromium carbides in the three bases of alloys, but not in lower quantities than for the HfC carbides, except in the carbon-richest iron-based alloy.

The high stability of the HfC carbides was observed in the 1200°C-aged microstructures. The HfC phase was generally almost unchanged in term of surface fraction (and even this one increased during the high temperature stage in the 0.50C-containing iron alloy). The behavior of the chromium carbides is more contrasted: they disappeared at high temperature in the high carbon cobalt and nickel alloys, their surface fraction decreased in the high carbon iron alloy and, inversely, increased in the low carbon nickel and iron alloys.

The morphology stability at high temperature of the HfC carbides was the best in the cobalt-based alloys, followed by the nickel-based ones. In contrast fragmented carbides were already observed in the iron-based alloys in their as-cast conditions, as the post-solidification cooling was sufficient to promote this loss of the script-like shape of these eutectic carbides. This can be a supplementary reason, after the high intrinsic hardness of a cobalt-chromium matrix, for a high room temperature hardness for the cobalt alloys, in the as-cast condition as well as in the aged state, by comparison with the nickel alloys and the iron alloys for similar carbides fractions.

## 5. Conclusion

HfC carbides demonstrated in this study a universal high stability since they precipitated at solidification instead chromium carbides and they globally remain rather stable at high temperature on rather long times. Superior to the TaC carbides in this field, especially in chromium-rich nickel-based alloys, they represent an interesting alternative way of chromium-rich cast superalloys reinforcement, also because their particularly efficient repartition (interdendritic) and shapes (script-like). Thus, despite the rather high cost and low availability of this element, it can be envisaged to substitute these carbides to chromium carbides and furthermore tantalum carbides in cast carbides-strengthened superalloys destined to very high temperature applications. However, it is of course preliminarily compulsory to verify the expected very good high temperature mechanical properties and resistance.

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