ISSN : 0974 - 7486 Volume 9 Issue 12

Trade Science Inc.

Materials Science

An Indian Journal

Full Paper

MSAIJ, 9(12), 2013 [453-458]

Hafnium carbides in cast chromium-rich refractory alloys. Part 3: Case of iron-based alloys

Patrice Berthod

Institut Jean Lamour (UMR 7198), Team 206 "Surface and Interface, Chemical Reactivity of Materials"University of Lorraine, Faculty of Science and Technologies B.P. 70239, 54506 Vandoeuvre-lès-Nancy, (FRANCE)

E-mail : Patrice.Berthod@univ-lorraine.fr

ABSTRACT

After having tested the metallurgical effect of the addition of hafnium in nickel-based and cobalt-based alloys in presence of carbon in the two first parts of this work, the same procedure was followed in this third and final part to complete the study by considering the case of iron-based alloys. Three Hf-added iron alloys, with the same contents in Cr, C and Hf as the previous Ni-based and Co-based alloys, were elaborated and metallographically characterized. Here too hafnium carbides tended forming instead chromium carbides, with mainly a script-like shape for the eutectic carbides and also some blocky carbides unfortunately tending to migrate outwards during solidification under the electromagnetic stirring. The hardening due to the presence of hafnium carbides previously seen for the nickel-based and cobalt-based alloys was not found for iron alloys by comparison with ternary alloys especially elaborated containing only chromium carbides, probably because of the loss of carbides in the ingot core due to the later phenomenon. Hafnium appeared thus as a more constant {MC carbide}-former element than tantalum, with maybe a better high temperature stability as earlier observed in cobalt-based alloys but which remains to be verified for the two other nickel and iron bases.

KEYWORDS

Hafnium carbides;
Iron alloys;
Microstructures;
Hardness;
Comparison with chromium carbides.

INTRODUCTION

After the nickel-based alloys and the cobalt-based ones, alloys based on iron (eventually together with nickel) and rich in chromium are a third important family of metallic materials able to resist both mechanical stresses at high temperature[1] and hot corrosion[2]. Such alloys can be successfully reinforced by MC carbides, as TaC tantalum carbides[3,4]. HfC carbides, which appear as especially stable at high temperature (as earlier seen in cobalt-based alloys[5]), have recently proved that they also can form in nickel-based[6] and cobalt-based simple ternary alloys[7]. However, despite its especially strong carbide-forming behaviour, hafnium carbide is curiously much less frequently considered than tantalum carbides for example to reinforce refractory alloys, notably iron-based alloys for which only rare scientific articles can be found. Indeed, iron-based alloys about which hafnium carbides can be cited – the most often among numerous other carbides (and even nitrides...) – are evocated essentially in the large compositions of alloys protected by patents: concerning bulk alloys[8-11] or coatings[12,13], for example.

In this third and final part of this study dealing with hafnium carbides in the more common metallic bases of alloys used for high temperature applications one will examine the metallurgical response of chromium-rich carbon-containing iron-based alloys to the introduction of significant amounts of hafnium. As for the nickel-based and cobalt-based alloys previously under consideration in the two first parts of this work, three {Fe-25wt%Cr}-based alloys were elaborated by equiaxed foundry under inert atmosphere, for three (wt.%C ; wt.%Hf) combinations, similar to the ones already considered in the two first parts. Metallographic characterization and hardness measurements will be realized, with comparison with the alloys of the two first HfC-containing alloys families.

EXPERIMENTAL DETAILS

The three Fe-25wt.%Cr alloys containing carbon and hafnium for achieving the formation of hafnium carbides in the microstructures were elaborated by targeting the following compositions: Fe-25Cr-0.25C-3.72Hf, Fe-25Cr-0.50C-3.72Hf and Fe-25Cr-0.50C-5.58Hf. Here too, four other alloys were additionally elaborated: a binary one (Fe-25Cr) and three ternary ones (Fe-25Cr-0.25C, Fe-25Cr-0.5C and Fe-25Cr-1.0C). This was done again for obtaining alloys containing chromium carbides for the same Fe-25Cr base with a rather large volume fraction range to allow comparisons of microstructure and hardness between the two types of carbides.

All these seven alloys were synthesized from pure elements (at least 99.9wt.% of purity) to obtain ingots of about 40g. Elaborations were achieved using here too the CELES High Frequency induction furnace, in which fusion, melting and solidification all occurred in the same water-cooled copper crucible under pure Argon (300 millibars).

Each ingot was cut using a metallographic saw. The obtained pieces (volume of about 0.5 cm^3) were embedded in a cold resin mixture, then grinded / polished with SiC papers (grit from 120 to 1200). After having been ultrasonically cleaned, the mounted samples were finely polished using a textile disk enriched with 1μm alumina particles.

The microstructure examinations were done using a Scanning Electron Microscope (SEM, JEOL JSM-6010LA) mainly in Back Scattered Electrons mode (BSE) while the general composition of the alloys (except carbon) was controlled with the same SEM by Energy Dispersion Spectrometry. Matrix and carbides were subjected to pinpoint measurements with the same apparatus.

Indentations were performed with a Testwell Wolpert apparatus in order to specify the Vickers hardness of the seven alloys (load: 30kg). Three values of hardness were obtained per alloy, allowing the calculation of the average value and of the standard deviation.

RESULTS AND DISCUSSION

SEM examination of the obtained microstructures

The microstructures of the binary alloy and of the three ternary ones are illustrated in Figure 1. If the first alloy (Fe-25Cr) is free of carbides while the three other alloys contain carbides with a surface fraction logically increasing when the targeted carbon content increases, one can also see that the matrix may be double-phased. This is particularly evident in the 0.25wt.%C and 0.50wt.%C-containing alloys in which there are areas a little brighter than the rest of the matrix. Additional EDS pinpoint measurements showed that the chromium/iron balance tends to be different between the two types of matrix. This is probably due to the co-existence of the high temperature austenitic FCC form and of the low temperature ferritic BCC form. Further X-Ray Diffraction investigations will be of a good help to better characterize these microstructures.

For the three alloys containing carbon, the carbides having appeared during solidification are obviously chromium carbides. They seem forming a eutectic compound with the matrix, although the two phases may be less mixed (or much finer) than in the corresponding nickel-based and cobalt-based alloys of the two first parts of this work. These carbides are all interdendritic.

The microstructures of the three hafnium-containing iron-based alloys are presented in Figure 2. The Back Scattered Electrons mode allowed evidencing the HfC carbides in these SEM micrographs (white particles in all alloys) as well as the chromium carbides in the two alloys in which there are present: the two 0.50wt.%C-containing alloys. In the three alloys, as in the Hf-containing cobalt alloys studied in the second part of this work, the hafnium carbides obviously formed with two shapes: a blocky one (maybe the first solid to appear before the dendritic matrix) and a eutectic one (script-like).

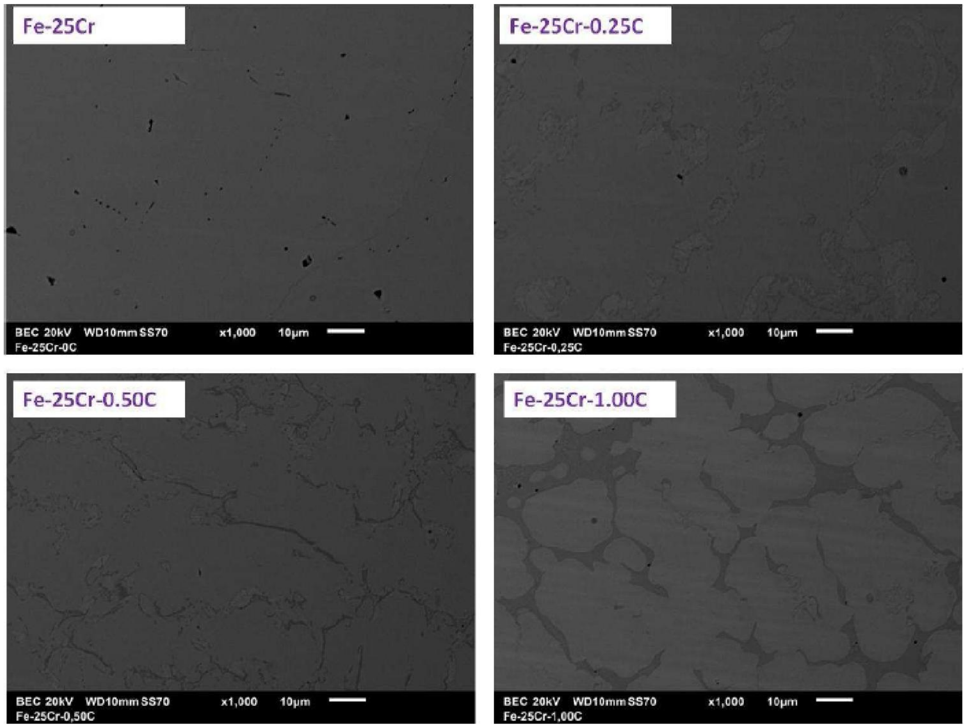


Figure 1: Microstructures of the four Fe-Cr (-C) alloys (SEM, Back Scattered Electrons mode)

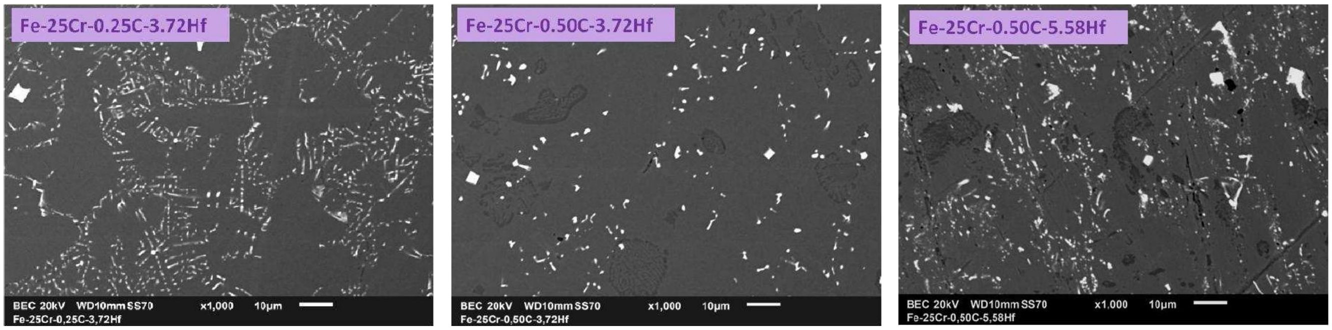


Figure 2: Microstructures of the three Fe-Cr-C-Hf alloys (SEM, Back Scattered Electrons mode)

SEM/EDS measurements of the global and local chemical compositions of the alloys

The general and matrix chemical compositions of the alloys measured by EDS are displayed in TABLE 1 for the Fe-Cr (-C) alloys and in TABLE 2 for the Fe-Cr-C-Hf alloys.

The targeted contents in chromium were rather respected in the binary and ternary alloys, even if the measured Cr contents are slightly higher than the targeted 25wt.%Cr. The chromium content in the matrix logically decreases when the carbon content in the alloy increases, since a greater part of chromium is then involved in the formation of the carbides.

In the Hf-containing alloys too the chromium content was rather well respected. This is also true for the hafnium contents on the two low-Hf alloys as well as in the high-Hf one. The chromium content in the matrix of the {chromium carbides}–free 0.25wt.%C-containing alloy is rather high by comparison with the one of the two other alloys which present chromium carbides in addition to the hafnium carbides. Concerning hafnium, accordingly with what was observed in the matrixes of

TABLE 1: General and matrix chemical compositions of the Fe-25Cr(-C) alloys

Alloy	Chromium	Carbon*
Fe-25Cr	26.04	0*
Fe-25Cr-0.25C	26.16	0.25*
Fe-25Cr-0.50C	26.24	0.50*
Fe-25Cr-1.00C	26.28	1.00*
Matrix of the alloy	**Chromium**	
Fe-25Cr	(26.04)	
Fe-25Cr-0.25C	25.47 ±0.45	
Fe-25Cr-0.50C	24.52 ±0.95	
Fe-25Cr-1.00C	22.61 ±0.68	

(EDS, wt.%, normalized at 100%; *: not measured and supposed to be respected)

the Hf-containing nickel-based alloys and cobalt-based alloys, this element seems here too totally absent in the matrixes of these iron-based alloys.

By examining the outer part of the ingots (Figure 3) it appears that, as for the Hf-containing cobalt-based alloys studied in the second part of this work, a rather significant part of HfC carbides have migrated towards the surface of the liquid domain during its early solidification. This may reveal that a part of the HfC carbides effectively precipitated very early during the solidification, before that the dendritic matrix network has appeared or at least was sufficiently developed to obstruct such migration. Such phenomenon can be responsible to the slight decrease in hafnium content in the alloy core. This can be the reason of the curious apparent lower surface fraction of HfC carbides in the microstructures of the two carbon-richest alloys by comparison with the Fe-25Cr-0.25C-3.72Hf alloy, the interdendritic {HfC + matrix} eutectic compound of which is paradoxically much more present. In the case of this later alloy it is possible that the dendritic structure early developed and efficiently inhibited the tendency of outward migration of the early HfC carbides.

TABLE 2: General and matrix chemical compositions of the Fe-25Cr-C-Hf alloys

Alloy	Chromium	Hafnium
Fe-25Cr-0.25C-3.72Hf	25.71	3.87
Fe-25Cr-0.50C-3.72Hf	25.59	3.46
Fe-25Cr-0.50C-5.58Hf	27.23	4.85
Matrix of the alloy	**Chromium**	**Hafnium**
Fe-25Cr-0.25C-3.72Hf	26.74 ±0.09	0 ±0
Fe-25Cr-0.50C-3.72Hf	25.74 ±0.87	0 ±0
Fe-25Cr-0.50C-5.58Hf	25.67 ±1.44	0.10 ±0.17

(EDS, wt.%, normalized at 100%; carbon: not measured and supposed to be respected)

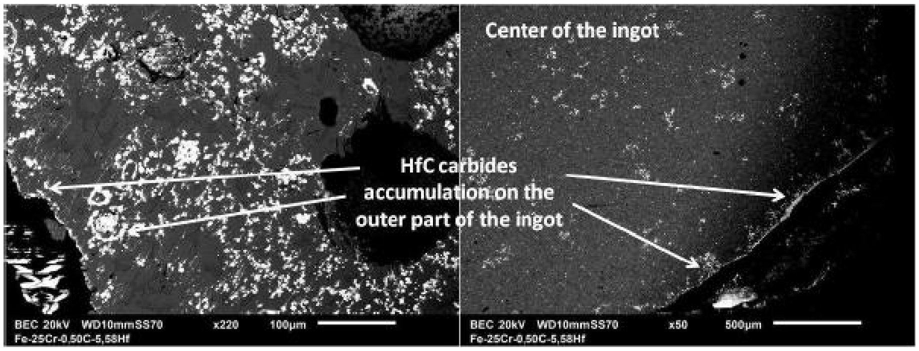
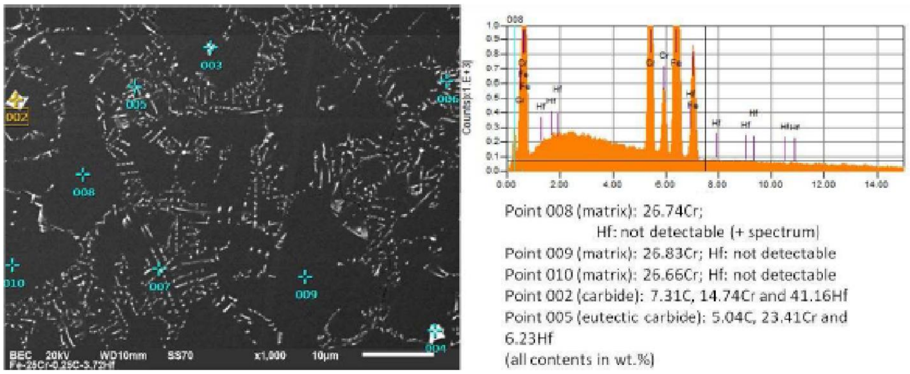


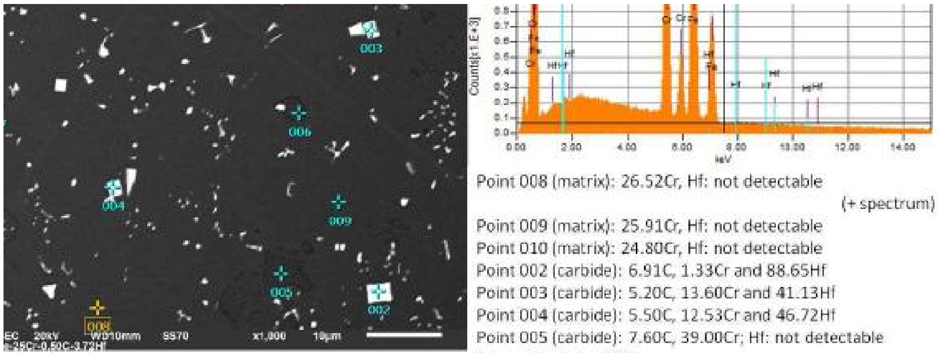
Figure 3: Early HfC carbides rejected in the outer part of the ingot when it was still melted



Point 008 (matrix): 26.74Cr;
Hf: not detectable (+ spectrum)
Point 009 (matrix): 26.83Cr; Hf: not detectable
Point 010 (matrix): 26.66Cr; Hf: not detectable
Point 002 (carbide): 7.31C, 14.74Cr and 41.16Hf
Point 005 (eutectic carbide): 5.04C, 23.41Cr and 6.23Hf
(all contents in wt.%)

Figure 4: Fe-25Cr-0.25C-3.72Hf alloy: locations of the pinpoint EDS measurements and the results obtained (Fe: rest)

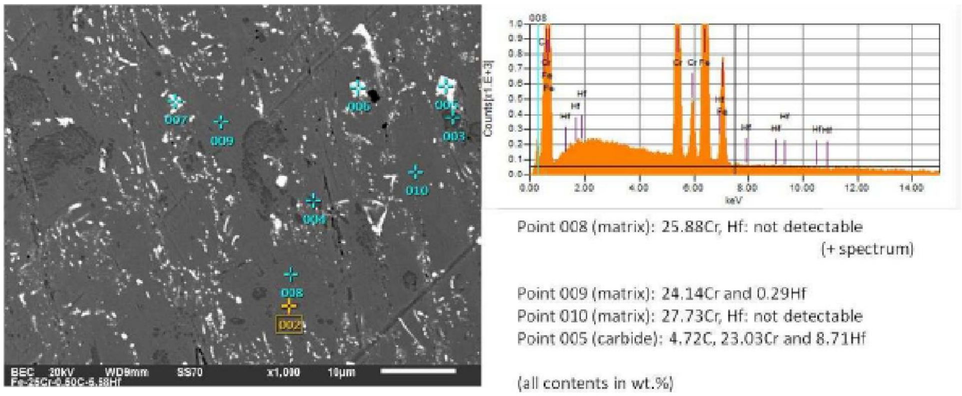
Figure 4 (respectively Figure 5 and Figure 6) presents some examples of pinpoint EDS measurements in the Fe-25Cr-0.25C-3.72Hf (resp. Fe-25Cr-0.50C-3.72Hf and Fe-25Cr-0.50C-5.58Hf) alloy, the locations of measurement and the corresponding values. Hf is effectively often not detectable in matrix while the bright carbides and the dark ones are respectively rich in hafnium and in chromium (and all of them in carbon).



Point 008 (matrix): 26.52Cr, Hf: not detectable
(+ spectrum)

Point 009 (matrix): 25.91Cr, Hf: not detectable
Point 010 (matrix): 24.80Cr, Hf: not detectable
Point 002 (carbide): 6.91C, 1.33Cr and 88.65Hf
Point 003 (carbide): 5.20C, 13.60Cr and 41.13Hf
Point 004 (carbide): 5.50C, 12.53Cr and 46.72Hf
Point 005 (carbide): 7.60C, 39.00Cr; Hf: not detectable
(all contents in wt.%)

Figure 5: Fe-25Cr-0.50C-3.72Hf alloy: locations of the pinpoint EDS measurements and the results obtained (Fe: rest)



Point 008 (matrix): 25.88Cr, Hf: not detectable
(+ spectrum)

Point 009 (matrix): 24.14Cr and 0.29Hf
Point 010 (matrix): 27.73Cr, Hf: not detectable
Point 005 (carbide): 4.72C, 23.03Cr and 8.71Hf

(all contents in wt.%)

Figure 6: Fe-25Cr-0.50C-5.58Hf alloy: locations of the pinpoint EDS measurements and the results obtained (Fe: rest)

General commentaries

Thus, the {MC carbides}-former property of hafnium was here found again in a {Fe-25wt.%Cr}-base and the iron alloys with the same (or similar) contents in Cr, C and Hf as the nickel alloys and the cobalt alloys, subjects of the first and second parts of this study, present microstructures with hafnium carbides (and chromium carbides in some cases) which are similar to the ones previously encountered for the two first alloys families. Despite some differences about fractions and/or morphologies of the carbides, there are here much more common points between the three families, contrarily to what was earlier observed for the TaC carbides between {Co-30wt.%Cr}-based[15], {Ni-30wt.%Cr}-based[16] and {Fe-30wt.%Cr}-based[3] alloys with the same carbon and tantalum contents (TaC slightly more numerous in the Fe-based alloys than in the Co-based alloys, but much more than in the Ni-based alloys).

Concerning the mechanical properties it was preliminarily seen in this whole study that the hardness at room temperature was generally increased by the addition of hafnium and the resulting substitution of chro-

TABLE 3: Hardness values obtained for the seven alloys (average and the three different values)

Alloy	0wt.%C	0.25wt.%C	0.50wt.%	1.00wt.%
Fe-25Cr-xC	199 (200-202-194)	209 (210-207-211)	219 (223-223-211)	356 (357-360-351)
Fe-25Cr-xC-3.72Hf		169 (169-172-165)	173 (172-169-177)	
Fe-25Cr-xC-5.58Hf			185 (185-184-187)	

mium carbides by hafnium carbides which are known to be harder[14]. If this was here rather the contrary which was observed (for the iron alloys, Figure 7) consecutively to a severe Hf carbides migration outside, this was in contrast true for the nickel alloys[6] (Figure 8) and for the cobalt alloys[7] (Figure 9). This let think that the mechanical capabilities of such alloys are probably interesting at high temperature, field to which such alloys may be potentially considered.

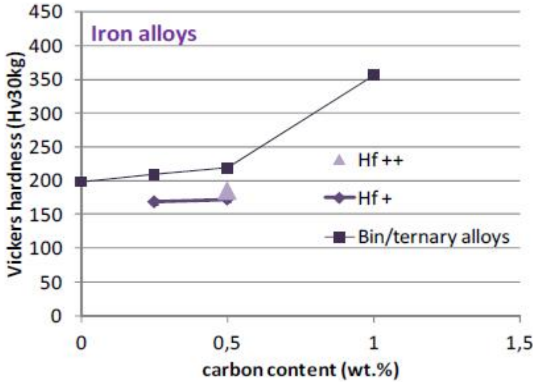


Figure 7: Hardness evolution of the iron alloys versus the carbon and hafnium contents

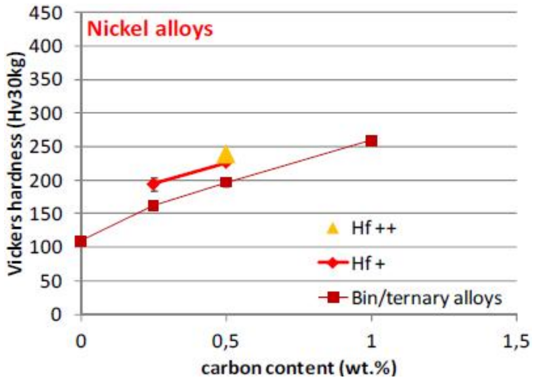


Figure 8: Hardness evolution of the nickel alloys versus the carbon and hafnium contents

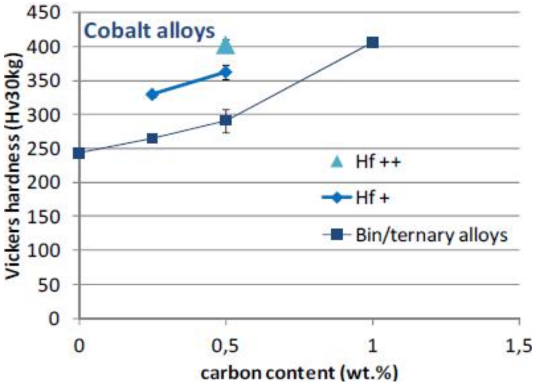


Figure 9: Hardness evolution of the cobalt alloys versus the carbon and hafnium contents

CONCLUSIONS

With this final part of this study of the hafnium carbides in alloys belonging to the three main families of metallic alloys for high temperature, one knows that hafnium carbides tend to easily appear in Cr-rich alloys, although that chromium is also a carbide-former element. The HfC carbides are mainly script-like eutectic carbides mixed with matrix in the interdendritic spaces, although some of them are blocky and tend to segregate outside the molten ingot before that solidification finishes. Known as much more stable than tantalum carbides in some cobalt-based alloys[5], it would be interesting to test their stability at high temperature in nickel-based and iron-based alloys, in order to see whether their potential strengthening effect can be maintained at a high level over long times.

REFERENCES

[1] M.J.Donachie, S.J.Donachie; Superalloys: A Technical Guide, 2nd Edition, ASM International, Materials Park, **(2002)**.
[2] J.Young; High Temperature Oxidation and Corrosion of Metals, Elsevier, Amsterdam, **(2008)**.
[3] P.Berthod, Y.Hamini, L.Aranda, L.Héricher; Calphad, **31**, 351 **(2007)**.
[4] P.Berthod, Y.Hamini, L.Héricher, L.Aranda; Calphad, **31**, 361 **(2007)**.
[5] P.Berthod; Journal of Alloys and Compounds, **481**, 746 **(2009)**.
[6] P.Berthod; Materials Science: An Indian Journal, accepted paper.
[7] P.Berthod; Materials Science: An Indian Journal, accepted paper.
[8] R.Sifferlen, C.Guichard, J.C.Soret; patent FR 1969-9746 **(1969)**.
[9] A.Yanagimachi, J.Sugawara; patent JP 1971-46827 **(1971)**.
[10] T.Nishida, M.Yamamiya, S.Senda, T.Yamazaki; patent JP 1989-269053, **(1989)**.
[11] M.P.Brady, H.T.Lin; patent US 2005-224179 **(2005)**.
[12] C.Leconte; patent US 1998-210537 **(1998)**.
[13] R.Ray, D.W.Scott; patent US 2003-624497 **(2003)**.
[14] G.V.Samsonov; High-Temperature Materials- N°2: Properties index, Plenum Press, New York, **(1964)**.
[15] P.Berthod, S.Michon, L.Aranda, S.Mathieu, J.C.Gachon; Calphad, **27(4)**, 353 **(2003)**.
[16] P.Berthod, L.Aranda, C.Vébert, S.Michon; Calphad, **28**, 159 **(2004)**.