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Hafnium carbides in cast chromium-rich refractory alloys. Part 2: Case of cobalt-based alloys

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ABSTRACT

In this second part of a work dealing with the microstructure effect of hafnium in chromium-rich refractory alloys in presence of carbon, cobalt alloys were considered. Several weight percents of Hf were added to {Co-25Cr}-based alloys also containing 0.25 and 0.50wt.% of carbon. This led to the development of interdendritic HfC carbides forming a eutectic with the matrix, instead chromium carbides. The same behaviour as previously seen in the first part of this work about nickel alloys was then found again. As in the later alloys the repartition and morphology of these HfC carbides let think to good mechanical resistance at room temperature as well as at high temperature. Hardness at ambient temperature is enhanced by the presence of these HfC carbides, by comparison with the chromium carbides existing in the same alloys in absence of Hf and also by comparison to HfC-containing nickel alloys of similar compositions.

KEYWORDS

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

INTRODUCTION

Hafnium, known for its effect on the high temperature oxidation and corrosion behaviour of refractory metallic alloys in general[1-3], was initially also considered as addition element in cobalt-based alloys for this purpose[4,5]. The influence of this element on the properties of cobalt alloys also concerned mechanical properties of bulk materials[6] less or more charged in HfC carbides (even higher than 20% in volume)[7], as well as of coatings[8]. If carbides – notably chromium carbides – are since several decades used for the mechanical strengthening of cobalt alloys in general (bulk materials or coatings)[9-12] and especially cobalt-based superalloys[13], hafnium carbides were less frequently considered as mechanical reinforcement of refractory alloys and superalloys for high temperature applications[14-16].

In this second part of the present work concerning the possibility of presence of hafnium carbides in chromium-rich refractory alloys, the case of cobalt-based alloys was examined. Hafnium was added in a Co-25Cr (wt.%) base together with carbon in order to favour, during the elaboration by foundry, the eventual precipitation of hafnium carbides during the solidification of the studied cobalt alloys. As previously done in the case of nickel alloys[17], three hafnium-containing chromium-rich cobalt-based alloys were synthesised by foundry under inert atmosphere and characterized in metallography and hardness with comparison to ternary Co-25Cr-C alloys presenting the same carbon contents, especially elaborated.

EXPERIMENTAL DETAILS

The experimental procedure applied in this second part is similar to the one followed in the first part. This can be summarized as follows. First, three Co-25wt.%Cr alloys added with carbon and hafnium were elaborated under inert atmosphere (300 mbars of pure Ar) using a High Frequency induction furnace (CELES) by targeting the following compositions: Co-25Cr-0.25C-3.72Hf, Co-25Cr-0.50C-3.72Hf and Co-25Cr-0.50C-7.44Hf (hafnium carbides favoured by these Hf and C contents), as well as four additional alloys (chromium carbides favoured by the presence of the single Cr element as carbide-former element, except for the binary alloy): a binary Co-25Cr one and three ternary Co-25Cr-0.25C, Co-25Cr-0.5C and Co-25Cr-1.0C ones, for microstructure and hardness comparisons between the two types of carbides. All alloys were synthesized from pure elements (99.9wt.% of purity, at least) in order to obtain 40g-ingots.

After cutting, parts of these ingots were embedded in a cold resin mixture and polished with SiC papers then a textile disk enriched with fine hard particles until obtaining a mirror-like surface. Microstructure examinations were done using a JEOL JSM-6010LA Scanning Electron Microscope. The general composition of the alloys (except carbon) was controlled by Energy Dispersion Spectrometry with additional pinpoint measurements in matrix and carbides. X-Ray Diffraction runs were performed using a Philips X'Pert Pro diffractometer. To finish, the Vickers hardness of each alloy was specified by three indentations performed with a load of 30kg.

RESULTS AND DISCUSSION

SEM examination of the obtained microstructures; XRD analysis results

Figure 1 presents the microstructures of the Co-25Cr binary alloy and of the three Co-25Cr-xC ternary alloys. The first one appears being single-phased when observed with the SEM in BSE mode. In fact, as revealed by the first XRD spectra shown in Figure 2, there are two phases: the austenitic chromium-containing solid solution of cobalt (typical of high temperature) and the hexagonal Cr-containing solid solution of cobalt (typical of low temperature). According to the binary Co-Cr phase diagram, the FCC$\rightarrow$HCP allotropic transformation should occur near 900°C but this was obviously not totally achieved, probably because of the fast solid state cooling in the water-cooled copper crucible of the furnace.

The low carbon Co-25Cr-0.25C alloy does not contain many carbides. Chromium carbides become more visible in the medium carbon Co-25Cr-0.50C alloy and especially in the high carbon Co-25Cr-1.0C alloy. They form a eutectic with matrix, present in the interdendritic spaces. The carbides obtained in these ternary cobalt-based alloys are obviously less present than in the ternary nickel-based alloys studied in the first part of this work, despite that the chromium and carbon contents are the same between the two families of studied alloys. Even for the two later alloys, XRD did not allow the determination of the nature of these carbides since their volume fractions were obviously too low. It was then not possible to know whether these carbides are $Cr_{23}C_6$ or Cr_7C_3 (as this can be expected for such Cr/C ratio in a cobalt-based alloy). In contrast X-Ray Diffraction allows seeing that the matrix is here too constituted of two types: FCC and HCP. One can notice that it seems that the FCC part of matrix becomes more and more important (and the HCP part less and less present) when the carbon content in the alloy increases. For 1wt.%C the Co-25Cr-C alloy seems still wholly austenitic: only the peaks corresponding to the FCC type are present.

Figure 3 presents the microstructures of the three hafnium-containing alloys. The first one (Co-25Cr-0.25C-3.72Hf) is constituted of a dendritic matrix, and of interdendritic carbides forming a eutectic with the matrix which would be hafnium carbides as suggested by their white colour (high average atomic number). Similar microstructures are observed for the second alloy (Co-25Cr-0.50C-3.72Hf) - except in its case the presence of some rare additional chromium carbides - and for the third alloy (Co-25Cr-0.50C-7.44Hf) which is {chromium carbides}-free (as the first alloy) and much more rich in hafnium carbides than the second

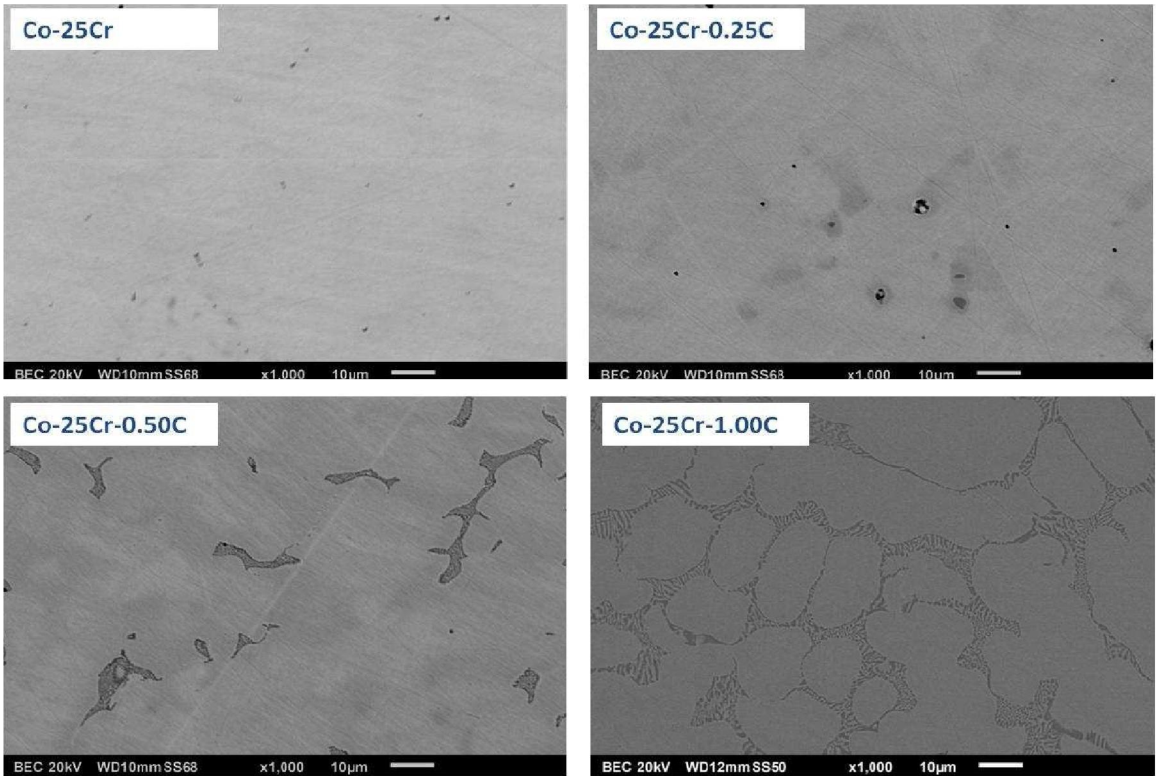
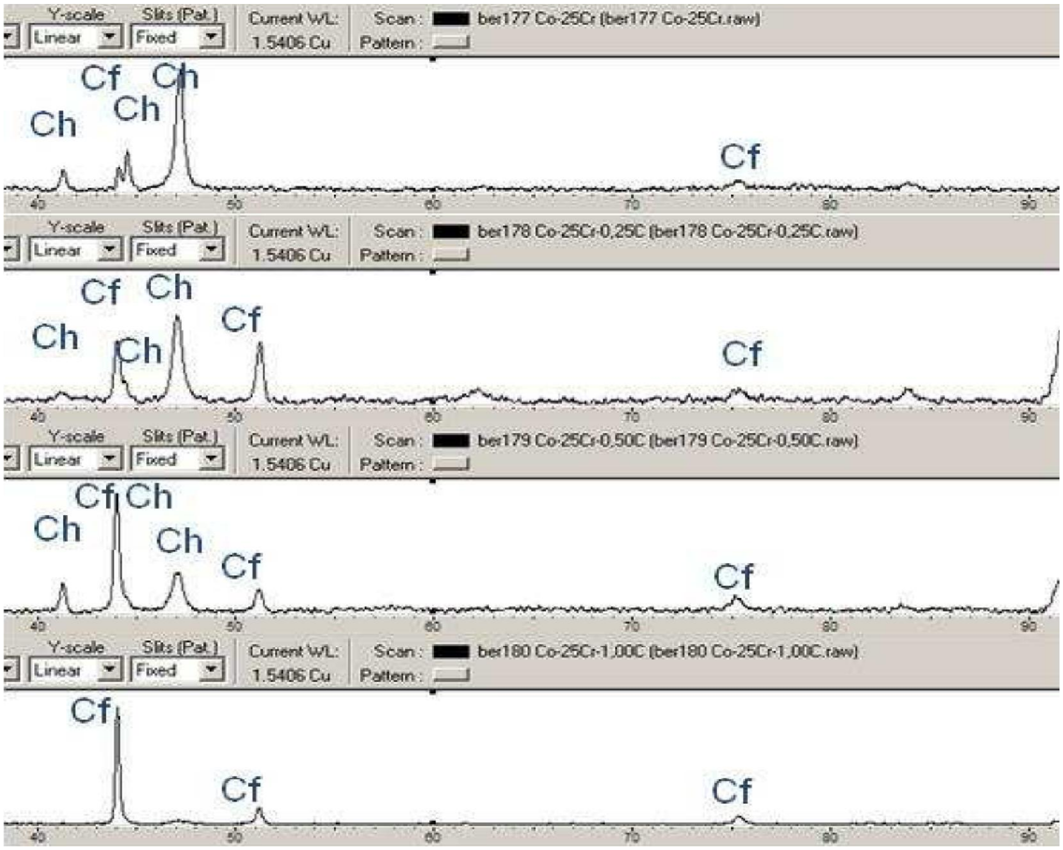


Figure 1 : Microstructures of the four Co-Cr(-C) alloys (SEM, Back Scattered Electrons mode).


Y-scale Linear Slits (Pat.) Fixed Current WL: 1.5406 Cu Scan : ber177 Co-25Cr (ber177 Co-25Cr.raw) Pattern :

Y-scale Linear Slits (Pat.) Fixed Current WL: 1.5406 Cu Scan : ber178 Co-25Cr-0,25C (ber178 Co-25Cr-0,25C.raw) Pattern :

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Figure 2 : The XRD spectra obtained for the four Co-Cr(-C) alloys (Cf: FCC cobalt-chromium matrix, Ch: HCP cobalt-chromium matrix).

alloy. The XRD spectra shown in Figure 4 are a little difficult to interpret since the peaks corresponding to the HfC carbides are more or less superposed with some of the peaks of the FCC matrix and of the HCP matrix. However it seems that the HfC are effectively present and also that the matrix tends to be less HCP and more FCC when the carbon content and/or the hafnium content increase.

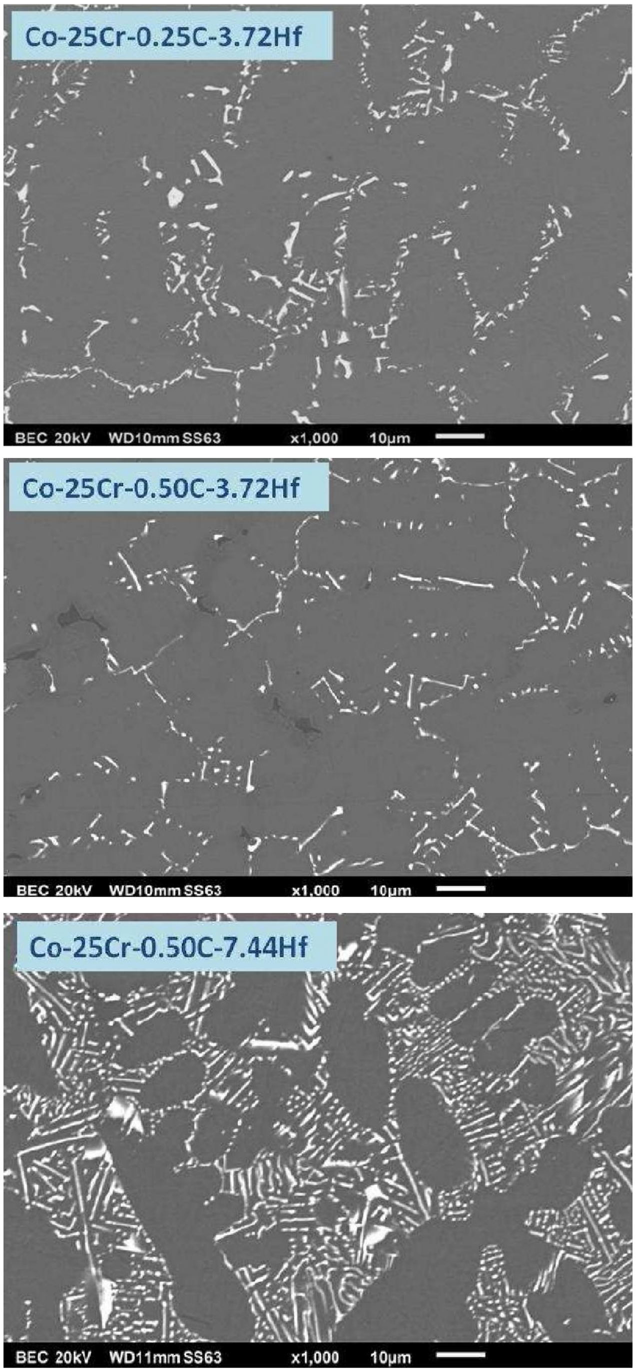


Figure 3 : Microstructures of the three Co-Cr-C-Hf alloys (SEM, Back Scattered Electrons mode).

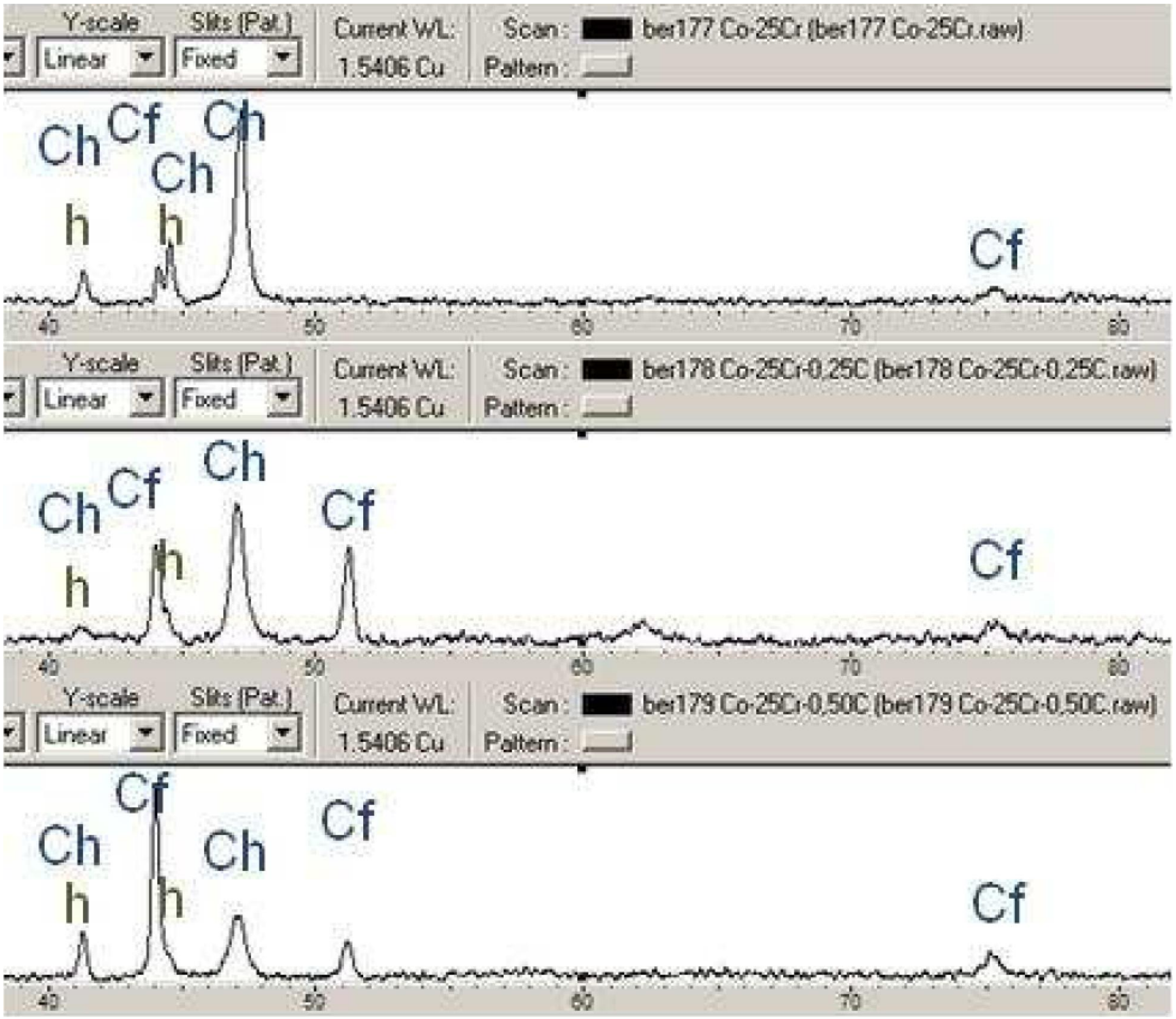
SEM/EDS measurements of the global and local chemical compositions of the alloys

The alloy chemical composition and the matrix chemical composition of the alloys measured by EDS are given in TABLE 1 for the Co-Cr(-C) alloys and in TABLE 2 for the Co-Cr-C-Hf alloys. The measurement locations in matrix as well as in carbides can be seen in Figure 5 for the Co-25Cr-0.25C-3.72Hf alloy, in Figure 6 for the Co-25Cr-0.50C-3.72Hf alloy and in Figure 7 for the Co-25Cr-0.50C-7.44Hf alloy.

The chromium contents in the Co-Cr(-C) alloys tends to be a little higher than the targeted ones, especially for the Co-25Cr-1.0C alloy (more than 2wt.%Cr more). This is also true for the three Co-Cr-C-Hf alloys. In the latter ones, the hafnium contents also appear being a little higher than the targeted values. Concerning the chemical compositions of the matrixes of the ternary alloys, the higher the carbon content the lower the chromium content. As for the nickel alloys of the first part of this work, this is due to the formation of more and more carbides involving an increasing part of the chromium of the alloy. The chromium content evolution in the matrix of the HfC-containing alloys in inverse since it increases when the volume fraction of the Cr-free HfC carbides increases, as is to say when the carbon content and/or the hafnium content increase. The hafnium content in the matrixes of the later alloys is very low, as already seen in the nickel alloys of the first part of this work. The average values of the three matrix Hf contents being of the same order of magnitude as the corresponding standard deviation, on can almost think that hafnium is totally absent in the matrix, and that the not-zero values may be due to neighbor carbides just under the surface.

TABLE 1 : General and matrix chemical compositions of the Co-25Cr(-C) alloys (EDS, wt.%, normalized at 100%; *: not measured and supposed to be respected).

Alloy	Chromium	Carbon*
Co-25Cr	25.00	0*
Co-25Cr-0.25C	25.19	0.25*
Co-25Cr-0.50C	25.90	0.50*
Co-25Cr-1.00C	27.29	1.00*
Matrix of the alloy :	**Chromium**	
Co-25Cr	(25.00)	
Co-25Cr-0.25C	24.22 ± 1.03	
Co-25Cr-0.50C	23.79 ± 0.76	
Co-25Cr-1.00C	22.38 ± 0.24	



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Y-scale: Linear
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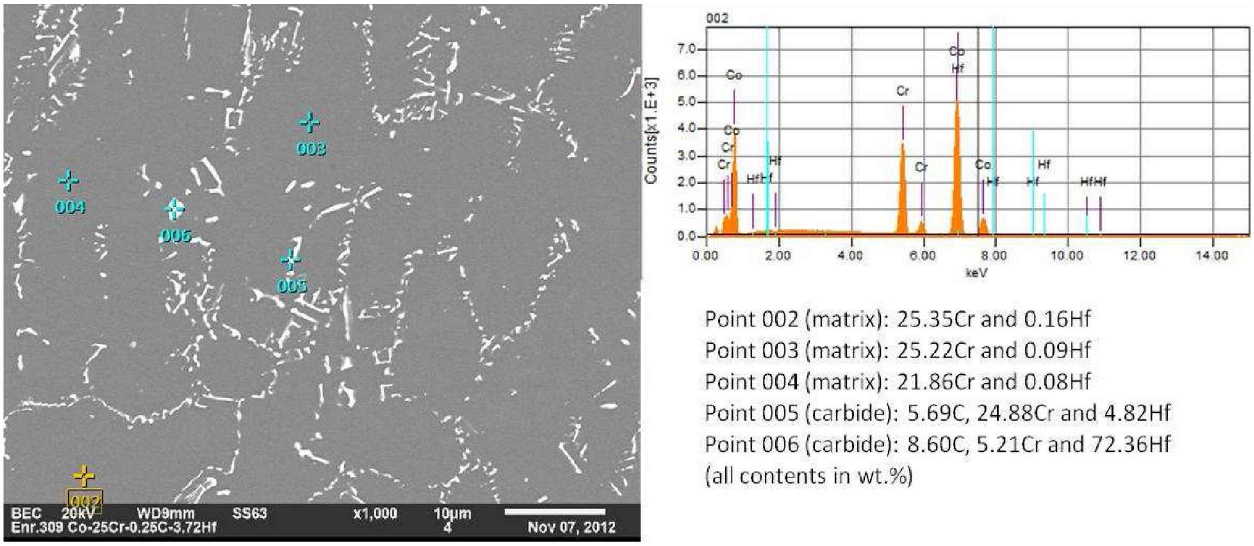
Scan: ber178 Co-25Cr-0.25C (ber178 Co-25Cr-0.25C.raw)
Pattern:

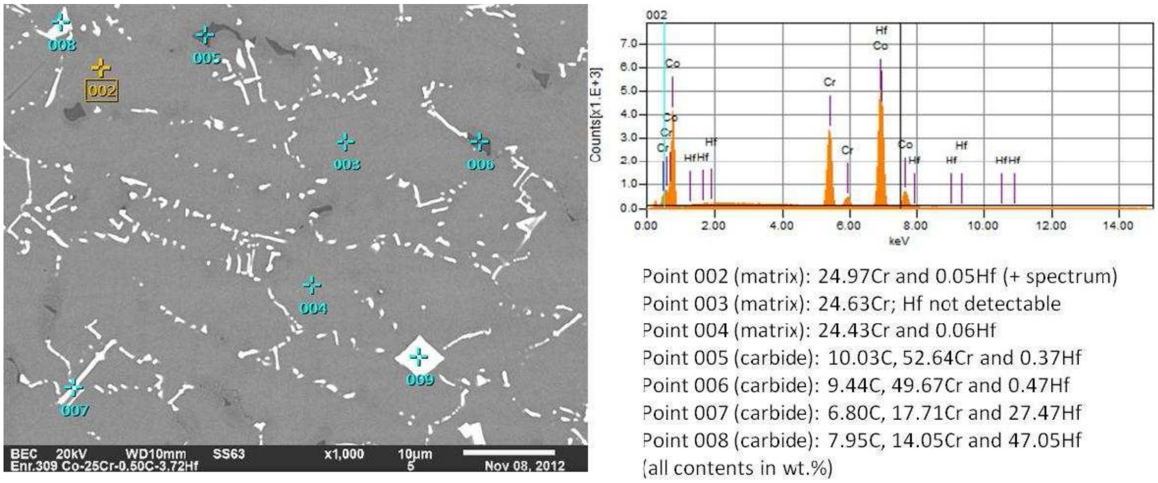
Y-scale: Linear
Slits (Pat.): Fixed
Current WL: 1.5406 Cu
Scan: ber179 Co-25Cr-0.50C (ber179 Co-25Cr-0.50C.raw)
Pattern:

Figure 4 : The XRD spectra obtained for the four Co-Cr-C-Hf alloys (Cf: FCC cobalt-chromium matrix, Ch: HCP cobalt-chromium matrix, h: HfC carbides).



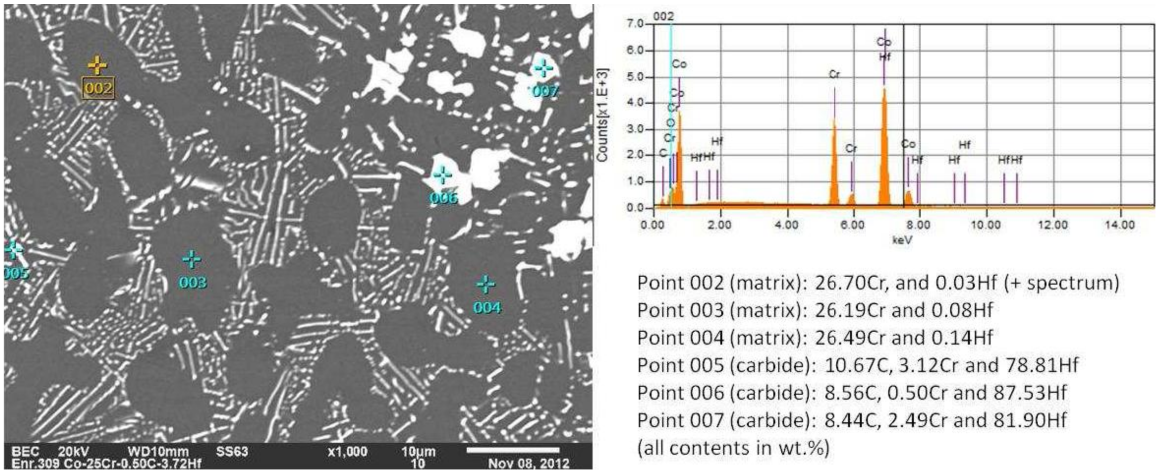
Point 002 (matrix): 25.35Cr and 0.16Hf
Point 003 (matrix): 25.22Cr and 0.09Hf
Point 004 (matrix): 21.86Cr and 0.08Hf
Point 005 (carbide): 5.69C, 24.88Cr and 4.82Hf
Point 006 (carbide): 8.60C, 5.21Cr and 72.36Hf
(all contents in wt.%)

Figure 5 : Co-25Cr-0.25C-3.72Hf alloy: locations of the pinpoint EDS measurements and the results obtained (Co: rest).



Point 002 (matrix): 24.97Cr and 0.05Hf (+ spectrum)
Point 003 (matrix): 24.63Cr; Hf not detectable
Point 004 (matrix): 24.43Cr and 0.06Hf
Point 005 (carbide): 10.03C, 52.64Cr and 0.37Hf
Point 006 (carbide): 9.44C, 49.67Cr and 0.47Hf
Point 007 (carbide): 6.80C, 17.71Cr and 27.47Hf
Point 008 (carbide): 7.95C, 14.05Cr and 47.05Hf
(all contents in wt.%)

Figure 6 : Co-25Cr-0.50C-3.72Hf alloy: locations of the pinpoint EDS measurements and the results obtained (Co: rest).



Point 002 (matrix): 26.70Cr, and 0.03Hf (+ spectrum)
Point 003 (matrix): 26.19Cr and 0.08Hf
Point 004 (matrix): 26.49Cr and 0.14Hf
Point 005 (carbide): 10.67C, 3.12Cr and 78.81Hf
Point 006 (carbide): 8.56C, 0.50Cr and 87.53Hf
Point 007 (carbide): 8.44C, 2.49Cr and 81.90Hf
(all contents in wt.%)

Figure 7 : Ni-25Cr-0.50C-7.44Hf alloy: locations of the pinpoint EDS measurements and the results obtained (Co: rest).

TABLE 2 : General and matrix chemical compositions of the Co-25Cr-C-Hf alloys (EDS, wt.%, normalized at 100%; carbon: not measured and supposed to be respected).

Alloy	Chromium	Hafnium
Co-25Cr-0.25C-3.72Hf	25.51	3.81
Co-25Cr-0.50C-3.72Hf	25.59	3.88
Co-25Cr-0.50C-7.44Hf	25.82	8.78
Matrix of the alloy :	**Chromium**	**Hafnium**
Co-25Cr-0.25C-3.72Hf	25.14 ±0.79	0.11 ±0.04
Co-25Cr-0.50C-3.72Hf	24.68 ±0.27	0.04 ±0.03
Co-25Cr-0.50C-7.44Hf	26.46 ±0.26	0.08 ±0.06

The HfC carbides tend to be a little more present in the present cobalt alloys than in the previous nickel alloys for the {0.25C; 3.72Hf} and {0.50C; 3.72Hf} couples of carbon and hafnium weight contents, which allowed to better analyse by EDS the HfC carbides (Figure 4 and Figure 5). For the Hf-richer cobalt alloy this was easier again thanks to a Hf content higher than in the Hf-richer nickel alloy (targeted content of 7.44wt.% against 5.58wt.%). The chemical composition obtained by pinpoint EDS measurement clearly showed that the white carbides are effectively hafnium carbides (Figure 7: 82 to 88wt.% of Hf in these carbides). One can notice that the especially high content in Hf in the third cobalt alloy (7.4wt.% targeted, 8.8wt.% obtained) led to not only eutectic HfC carbides but also compact HfC particles. By examining the outer part of the corresponding ingot one can see that occurred during its elaboration a phenomenon similar to what happened in carbon-rich (then {chromium carbides}-rich) alloys earlier studied (ternary Ni-30Cr alloys[18] and Co-30Cr alloys[19] with up to 5wt.%C): the migration of the early formed carbides towards the outer part of the ingot (Figure 8), consecutively to the electromagnetic stirring. Thus, as alloy rather heavy charged in Hf carbides, the Co-25Cr-0.50C-7.44Hf alloy behaves during fusion and solidification as other alloys very rich in chromium carbides.

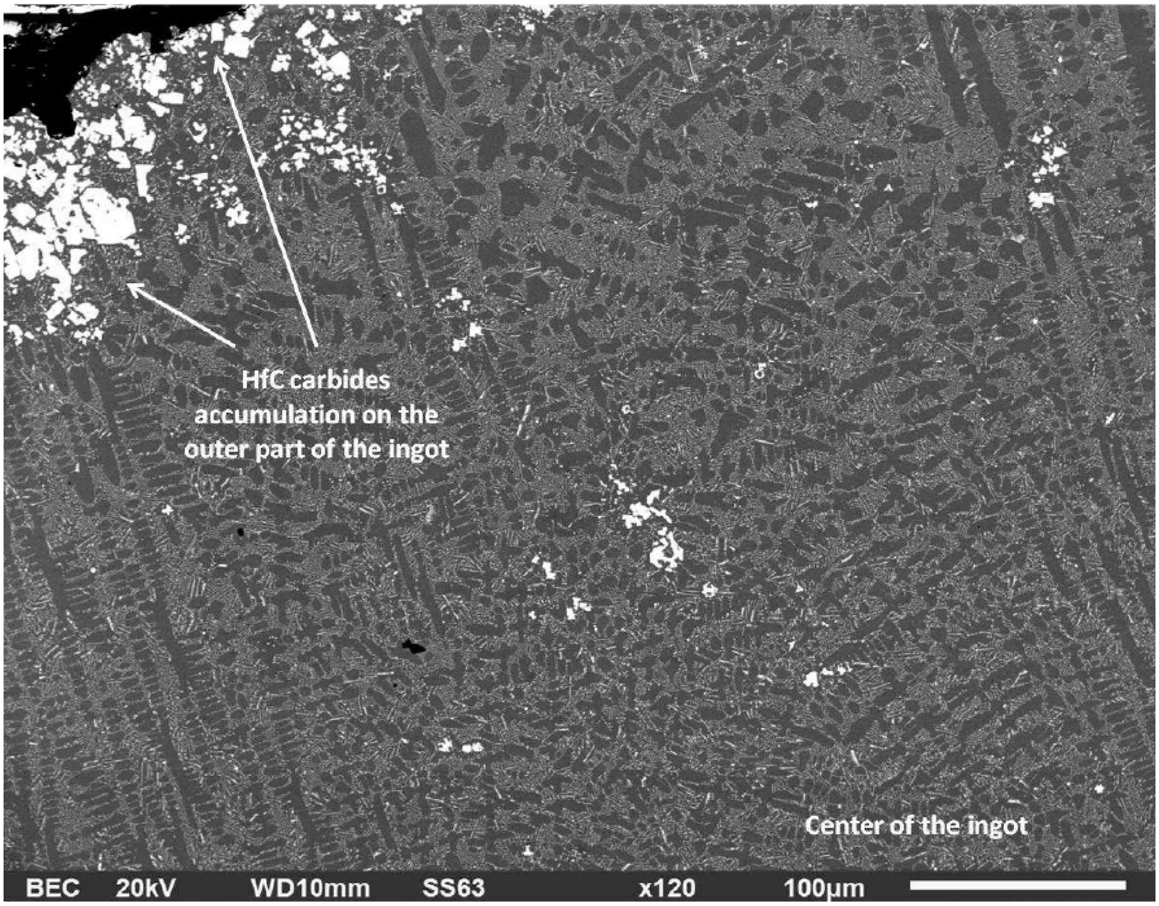


Figure 8 : Early HfC carbides rejected in the outer part of the ingot when it was still melted.

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.%
Co-25Cr-xC	244(242-242-247)	265(263-269-263)	291(281-281-311)	406(411-400-406)
Co-25Cr-xC-3.72Hf		329(331-326-331)	362(351-366-370)	
Co-25Cr-xC-7.44Hf			402(396-400-411)	

Hardness measurements

Vickers hardness was specified on the mounted samples, under a 30kg-load. TABLE 3 shows the obtained results. As for the nickel alloys of the first part of this study one can see that the hardness progressively increases with the carbon content for the Co-25Cr-xC alloys when x increases, and second that, for the same carbon content, the hardness becomes higher if the HfC carbides are present instead the chromium carbides. The highest hardness is reached for the Co-25Cr-0.50C-7.44Hf which is especially rich in HfC carbides.

General commentaries

In the chromium-rich cobalt-based alloys too, hafnium acts as a very strong carbide-former element, and, for a same Co-25Cr-xC base, all chromium carbides are replaced by hafnium carbides (except when there are more carbon atoms than hafnium atoms). This was already seen in previous studies also concerning cobalt-based alloys[14-16] in which they appeared as carbides-former stronger than not only Cr but also Ta, Nb or Zr. This behavior leads to the absence of Hf in the matrix, in contrast with tantalum for example which is always present with contents of about 1wt.% even if the Ta/C atomic ratio is equal to 1. Thanks to the especially great volume fraction of HfC carbides and of the very high hardness of the latter[20], as well as the intrinsic hardness of chromium-containing cobalt by comparison with chromium-containing nickel (hardness of Co-25Cr higher than the one of the Ni-25Cr: TABLE 3), the values of hardness obtained with the Co-25Cr-C-Hf alloys are significantly higher than the ones of the Ni-25Cr-C-Hf alloys.

CONCLUSIONS

The strong carbide-forming behaviour of hafnium, already observed in nickel alloys in the first part of this work is here found again in cobalt-based alloys for the same chromium and carbon contents. The eutectic type (and shape) of most of these HfC carbides may be very favourable to high mechanical resistance at high temperature notably, as this already led here to high hardness at room temperature. This exploration of hafnium forming HfC carbides in cast refractory alloys will be finished in a third part, this time concerning iron-based alloys[21].

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