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Hafnium carbides in cast chromium-rich refractory alloys. Part 1: Case of nickel-based alloys

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ABSTRACT

Hafnium, generally used for the improvement of the behaviour of the superalloys in high temperature oxidation, is also a strong carbide-former element. It forms MC carbides which can be extremely stable at very high temperature in some refractory alloys. In this work it was attempted to develop an interdendritic carbides network partly or wholly made of eutectic HfC carbides, in chromium-rich nickel-based quaternary alloys. Three Ni-25Cr-xC-yHf (contents in wt.%) with x belonging to {0.25; 0.50} and y $\in$ {3.7; 5.6} were elaborated by induction foundry under inert atmosphere, then characterized in the microstructure field and in hardness. The obtained microstructures effectively show dendritic matrixes and interdendritic HfC carbides forming a eutectic with the matrix, this type of carbides being either the single one or being mixed with eutectic chromium carbides. Thanks to the presence of these carbides with rather great volume fractions the hardness of the HfC-containing alloys is higher than the ones of ternary nickel alloys with the same chromium and carbon contents, also elaborated in this work for allowing such comparisons.

KEYWORDS

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

INTRODUCTION

The main family of metallic alloys used for high temperature applications is the nickel-based superalloys one. Many of them are resistant against oxidation by hot gases thanks to the presence of several percents of aluminium[1] and against creep deformation this being due to gamma prime (γ') precipitates which are of the general (Ni, Co, Fe)$_3$(Al, Ti, Ta, Nb) formulation[2]. However other nickel-based alloys, the most often met ones in the equiaxed cast family, contain several tens of chromium weight percents to resist hot corrosion in addition to high temperature oxidation, and these ones are mechanically reinforced rather by primary and/or secondary carbides. This is for example the case of alloys used for glass working[3]. If such alloys were often considered as bulk high temperature alloys several tens of years ago[4,5], they are now more considered as cermets-type {Cr_xC_y/Ni-based alloy, e.g. Cr_3C_2-NiCr} coatings deposited on substrates by high velocity oxy-fuel (HVOF)[7,8], detonation[9,10], thermal spray[11,12] or laser cladding[13].

In most cases the carbides added in a nickel-based matrix, as bulk materials as well as coating materials, are chromium carbides, with different possible stoichiometries $Cr_{23}C_6$, Cr_7C_3, Cr_3C_2 and even CrC, with possibly a limited substitution of chromium by another metallic carbide-former element (e.g. W in $Cr_{23}C_6$ carbides). Less frequently it was also attempted to introduce TaC carbides (e.g. recently[13]), which are among the most frequent MC carbides which can be encountered in superalloys.

The subject of this work is to try obtaining another type of MC carbides – the HfC carbides – in a nickel-chromium base alloy. This was done by elaborating by foundry way three Ni-25Cr alloys containing hafnium - in presence of carbon - with contents significantly higher than it is generally done when this element is added only for improving the resistance against high temperature oxidation. These alloys were metallographically characterized and their hardness specified, before comparison to the ones of binary and ternary nickel alloys with the same Ni-25Cr base and for similar carbon contents.

EXPERIMENTAL DETAILS

Procedure followed for elaborating the alloys

Three Ni-25wt.%Cr alloys containing carbon and hafnium for promoting the crystallisation of hafnium carbides in the microstructures were elaborated targeted compositions: Ni-25Cr-0.25C-3.72Hf, Ni-25Cr-0.50C-3.72Hf and Ni-25Cr-0.50C-5.58Hf. Four other alloys, binary (Ni-25Cr) and ternary (Ni-25Cr-0.25C, Ni-25Cr-0.5C and Ni-25Cr-1.0C), were also elaborated to obtain a volume fraction range of chromium carbides for a same Ni-25Cr alloy base, to allow microstructure and hardness comparisons between the two types of carbides.

All these seven alloys were synthesized from pure elements (99.9wt.% of purity, at least) for an ingot mass of around 40g each, using a CELES High Frequency induction furnace. Fusion, melting and solidification were performed in the same water-cooled copper crucible of the furnace, in a pure Argon atmosphere (300 millibars).

Metallographic preparation for obtaining samples for metallography and microstructure examinations

After total cooling down to ambient temperature each ingot was cut using a Delta Abrasimet Cutter (Buelher), the obtained pieces (volume of about 0.5 cm^3) being thereafter embedded in a cold resin mixture (resin CY230 + hardener HY956, from ESCIL). They were then grinded / polished with SiC papers (grit from 120 to 1200), ultrasonically cleaned and thereafter finely polished using a textile disk enriched with 1µm alumina particles.

The microstructure examinations were done using a JEOL Scanning Electron Microscope (SEM, model: JSM-6010LA) essentially in Back Scattered Electrons mode (BSE). The general composition of the alloys (except carbon) was controlled using the Energy Dispersion Spectrometry device equipping the SEM, while pinpoint measurements were also performed on matrix and carbides, using the same apparatus. To complete the microstructure characterization runs of X-Ray Diffraction (Philips X'Pert Pro diffractometer, wavelength: K_α of Cu, e.g. 1.5406 Angströms).

Hardness measurements

The indentations done in order to specify the hardness of the seven alloys were performed using a Testwell Wolpert apparatus. Three indentations were realized per alloy, in order to obtain an average value and to calculate a standard deviation. The load used was 30kg.

RESULTS AND DISCUSSION

SEM examination of the obtained microstructures; XRD analysis results

The as-cast microstructures of the four binary and ternary alloys are shown in Figure 1. The binary Ni-25Cr alloy is single-phased (chromium-containing FCC solid solution of nickel), according to the binary Ni-Cr phase diagram. Carbides – probably chromium carbides – appear in the low carbon Ni-25Cr-0.25C alloy, in which they are darker than matrix due to their lower average atomic number by comparison with the matrix. They are present with a greater surface fraction in the medium carbon Ni-25Cr-0.50C alloy, and the maximal fraction among these alloys is logically reached in the high carbon Ni-25Cr-1.0C alloy.

In the three last cases the chromium carbides obviously form a eutectic compound with the matrix and their acicular shape let think that they were of the Cr_7C_3

type at the solidification. One can guess that this high temperature variety of chromium carbides has been kept during the rather rapid cooling and did not transform into $Cr_{23}C_6$ carbides. This was unfortunately not really confirmed by the X-Ray Diffractions runs since the obtained spectra - presented in Figure 2 – show only the matrix peaks. The carbides were in too low quantities in these alloys (even in the high carbon one) to allow detecting them by XRD and then identifying their stoichiometry.

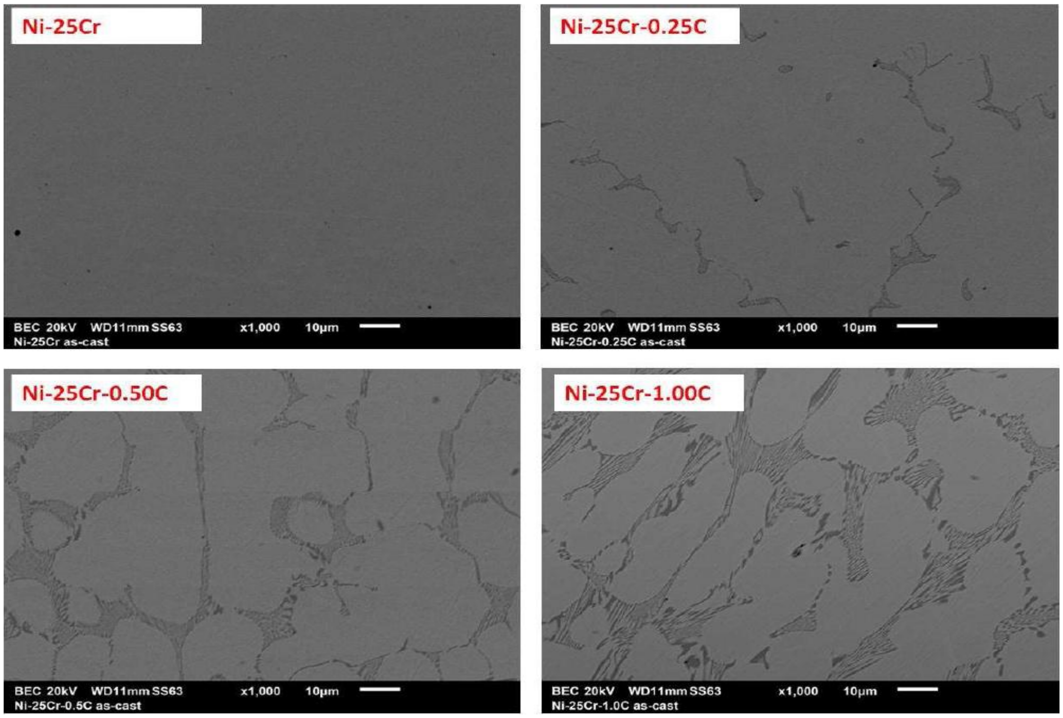
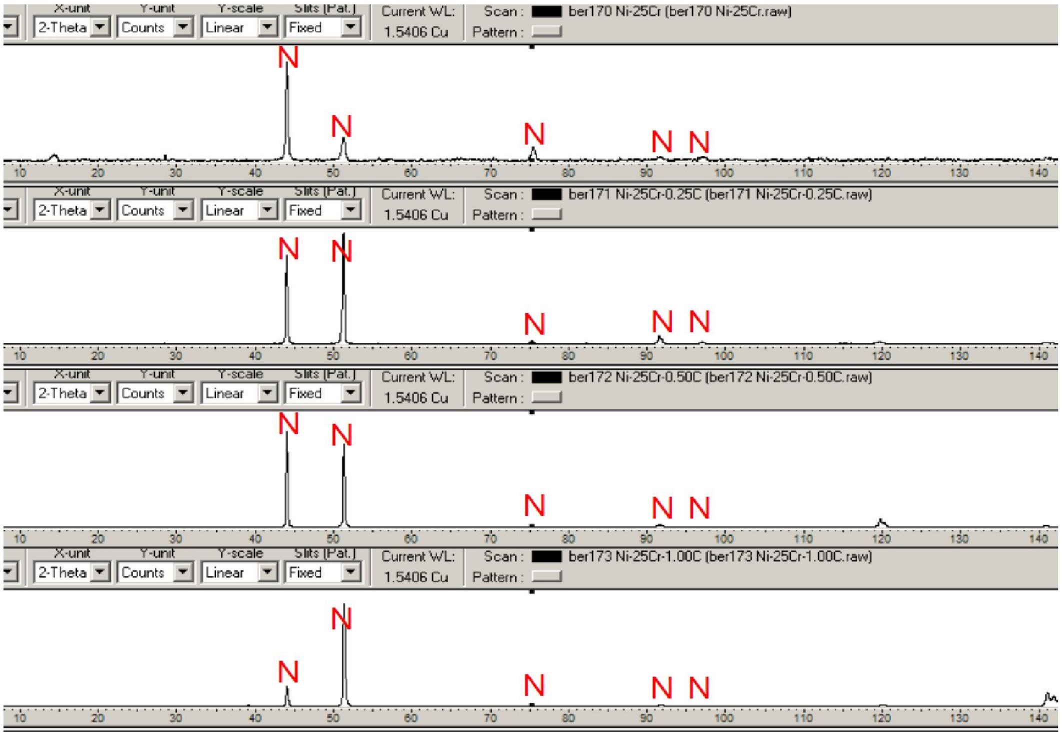


Figure 1 : Microstructures of the four Ni-Cr(-C) alloys (SEM, Back Scattered Electrons mode).


X-unit: 2-Theta; Y-unit: Counts; Y-scale: Linear; Slits [Pat.]: Fixed; Current WL: 1.5406 Cu; Scan: ber170 Ni-25Cr (ber170 Ni-25Cr.raw); Pattern:

X-unit: 2-Theta; Y-unit: Counts; Y-scale: Linear; Slits [Pat.]: Fixed; Current WL: 1.5406 Cu; Scan: ber171 Ni-25Cr-0.25C (ber171 Ni-25Cr-0.25C.raw); Pattern:

X-unit: 2-Theta; Y-unit: Counts; Y-scale: Linear; Slits [Pat.]: Fixed; Current WL: 1.5406 Cu; Scan: ber172 Ni-25Cr-0.50C (ber172 Ni-25Cr-0.50C.raw); Pattern:

X-unit: 2-Theta; Y-unit: Counts; Y-scale: Linear; Slits [Pat.]: Fixed; Current WL: 1.5406 Cu; Scan: ber173 Ni-25Cr-1.00C (ber173 Ni-25Cr-1.00C.raw); Pattern:

Figure 2 : The XRD spectra obtained for the four Ni-Cr(-C) alloys (N: nickel-chromium FCC matrix).

The microstructures of the three hafnium-containing alloys are presented in Figure 3. As for the three previous {chromium carbides}-containing Ni-25Cr alloys, their matrix is also dendritic with interdendritic spaces containing eutectic carbides. These carbides seem being only HfC in the first and third alloys.

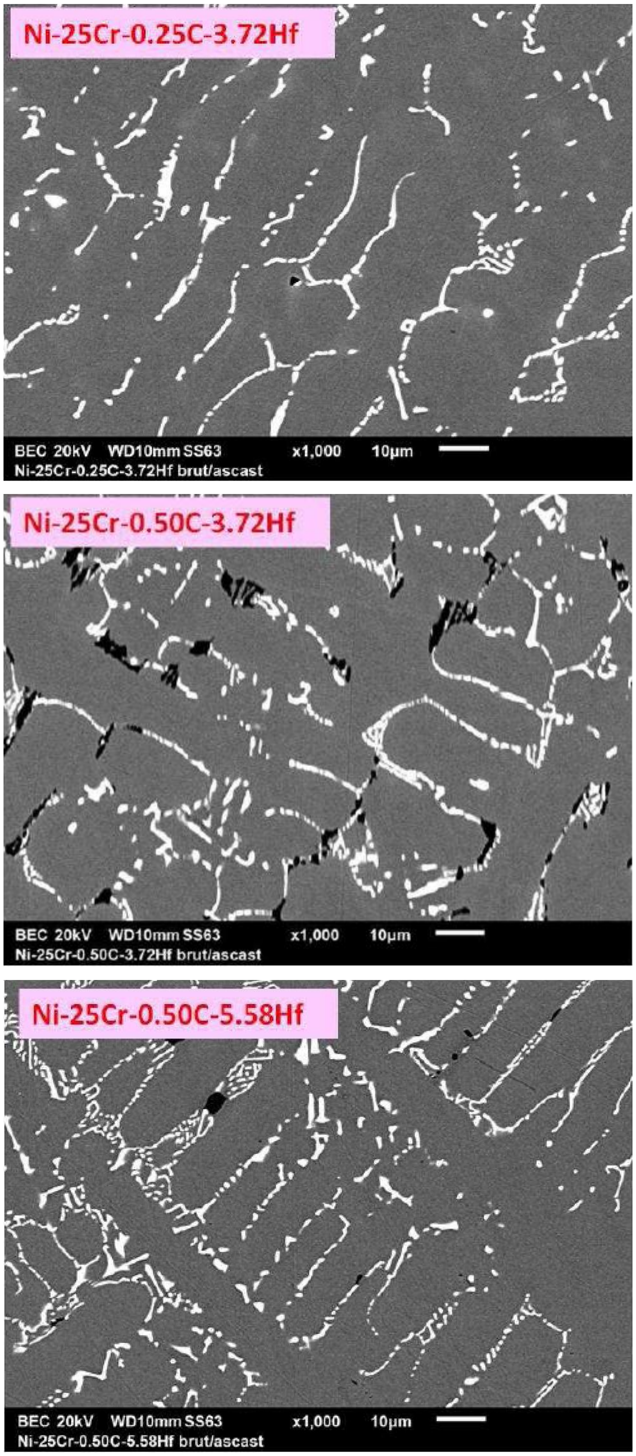


Figure 3 : Microstructures of the three Ni-Cr-C-Hf alloys (SEM, Back Scattered Electrons mode).

In contrast the second one seems containing not only hafnium carbides but also chromium carbides, with here too an acicular eutectic morphology typical of Cr_7C_3 carbides. XRD runs were also performed for these three quaternary alloys (Figure 4) and the obtained spectra show that new peaks are present with the ones corresponding to the FCC nickel-chromium matrix. These additional peaks effectively correspond to the HfC carbides. However no peak corresponding to chromium carbides was found.

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 Ni-Cr(-C) alloys and in TABLE 2 for the Ni-Cr-C-Hf alloys, the measurement locations being shown in Figure 4 for the Ni-25Cr-0.25C-3.72Hf alloy, in Figure 5 for the Ni-25Cr-0.50C-3.72Hf alloy and in Figure 6 for the Ni-25Cr-0.50C-5.58Hf alloy.

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

Alloy	Chromium	Carbon*
Ni-25Cr	25.00	0*
Ni-25Cr-0.25C	24.89	0.25*
Ni-25Cr-0.50C	26.23	0.50*
Ni-25Cr-1.00C	26.45	1.00*
Matrix of the alloy :	**Chromium**	
Ni-25Cr	(25.00)	
Ni-25Cr-0.25C	23.79 ±0.47	
Ni-25Cr-0.50C	22.74 ±0.17	
Ni-25Cr-1.00C	21.77 ±0.27	

The chromium contents in the Ni-25Cr(-C) alloys as well as in the Ni-25Cr-C-Hf alloys were seemingly rather well respected, even if the obtained values tend to be slightly higher than the targeted ones (less than 1wt.% higher). This is also true for the hafnium contents (here too less than 1wt.% higher but for a base content lower than for chromium). The chromium content in the matrix becomes logically lower and lower from the Ni-25Cr alloy (25.0 wt.%Cr) to the Ni-25Cr-1.00C alloy (26.5wt.%Cr) since the increasing volume fraction of carbides induces an increasing part of the total chromium involved in the carbides. The chromium contents in the matrixes of the three Hf-containing alloys are in contrast slightly higher than for the whole alloys since a volume part of the microstructure is constituted of chromium-free carbides (the HfC ones).

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

Alloy	Chromium	Hafnium
Ni-25Cr-0.25C-3.72Hf	25.70	4.40
Ni-25Cr-0.50C-3.72Hf	25.57	4.79
Ni-25Cr-0.50C-5.58Hf	25.32	6.64
Matrix of the alloy :	**Chromium**	**Hafnium**
Ni-25Cr-0.25C-3.72Hf	26.37 ±0.79	0.51 ±0.51
Ni-25Cr-0.50C-3.72Hf	25.60 ±0.36	0.21 ±0.15
Ni-25Cr-0.50C-5.58Hf	26.40 ±0.65	0.49 ±0.45

It seems that a small part of hafnium is contained in the matrixes of the three alloys (average value: 0.5wt.%) in the Ni-25Cr-0.25C-3.72Hf and Ni-25Cr-0.50C-5.66Hf alloys, and 0.20wt.% in the third one, but one can think that no hafnium is really present in the matrix. Indeed, the standard deviation values are of the same order of magnitude of the average value, this probably showing that the Hf content in matrix is very low and the highest values obtained for the Hf content in matrix results from the interaction of the electron beam with HfC present just under the surface. The variable character of the Hf content in matrix can be illustrated by the dispersion of the values given in Figure 4, Figure 5 and Figure 6.

In the same figures, the results of EDS pinpoint analyses on the carbides show that the hafnium content in carbides can be very high. But it is unfortunately true that it was difficult to keep an electron beam still focused on so small carbides all along acquiring and it was rarely possible to really specify the chemical composition of a carbide with an accuracy high enough.

Hardness measurements

Vickers indentations were performed on the mounted samples under a 30kg-load. The obtained results are given in TABLE 3. One can see first that the hardness continuously increases with the carbon content for the Ni-25Cr-xC alloys, and second that, for the same carbon content, the hardness is higher if the hafnium carbides are present instead chromium carbides, with in addition here too a dependence on the carbon content in the same direction.

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.%
Ni-25Cr-xC	109(109-110-109)	163 (163-160-165)	197 (191-198-202)	259 (263-257-257)
Ni-25Cr-xC-3.72Hf		194 (202-196-184)	226 (229-227-223)	
Ni-25Cr-xC-5.58Hf			239 (242-239-237)	

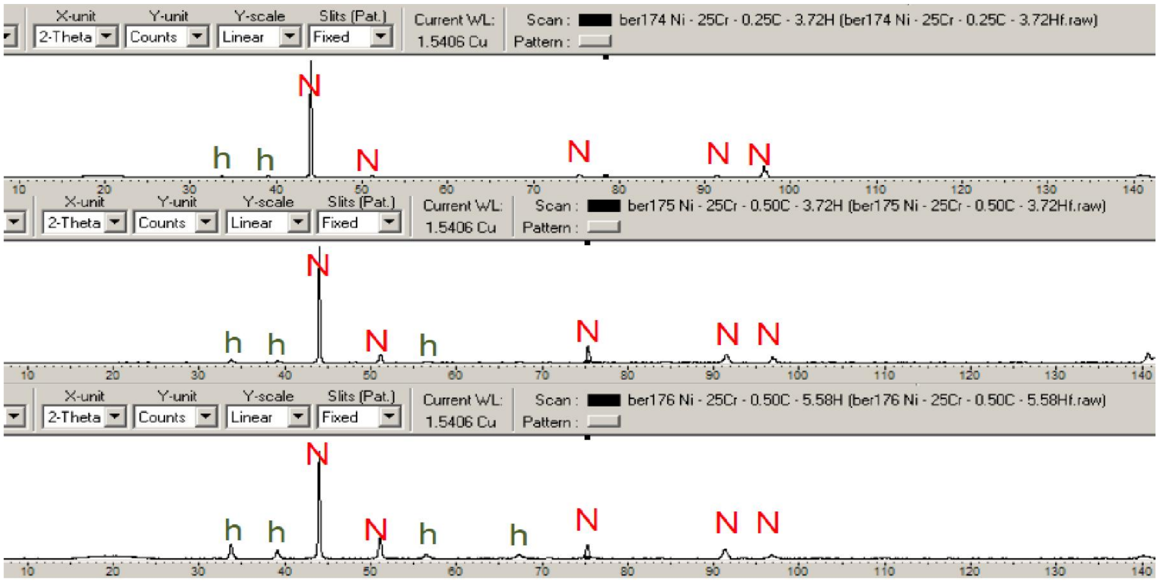
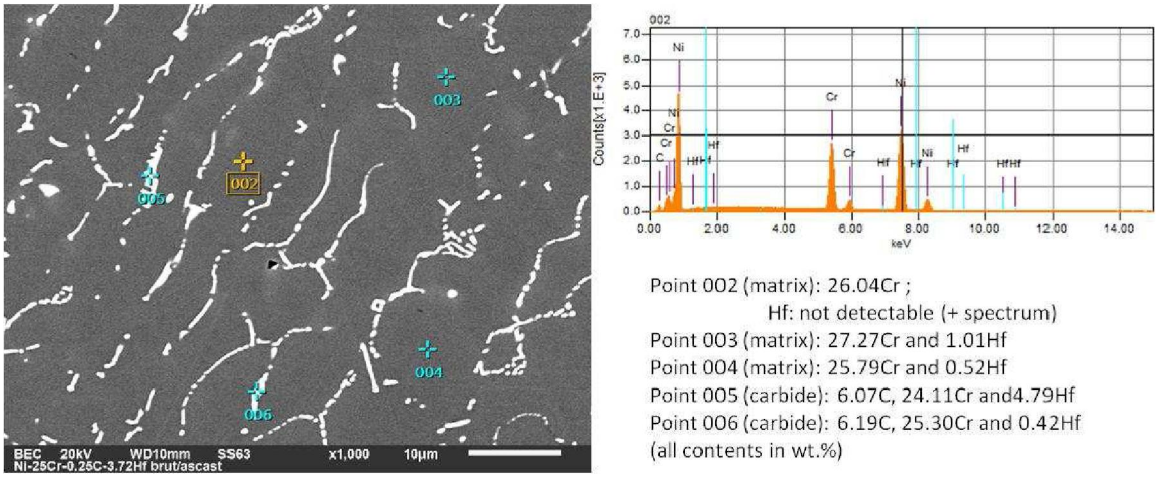
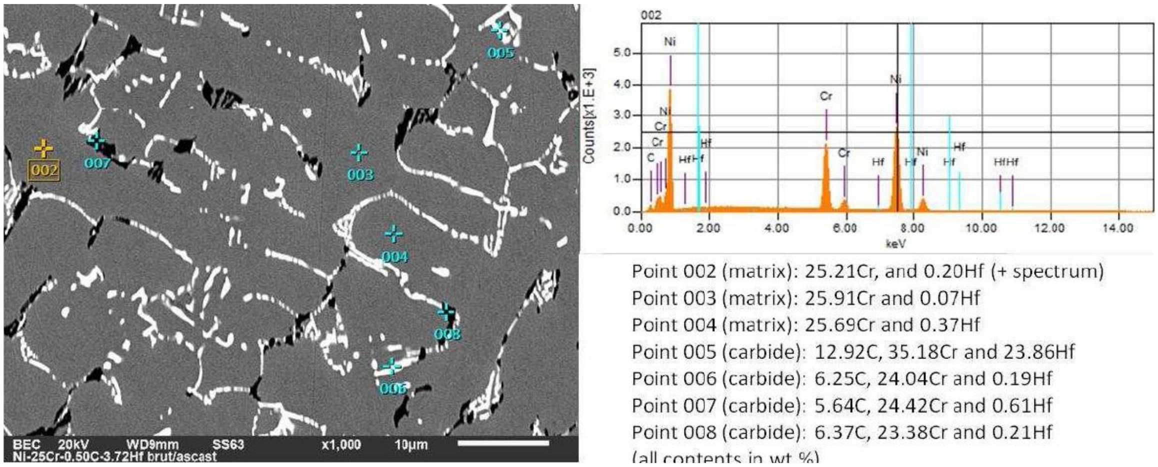


Figure 4 : The XRD spectra obtained for the four Ni-Cr(-C) alloys (N: nickel-chromium FCC matrix, h: HfC carbides).



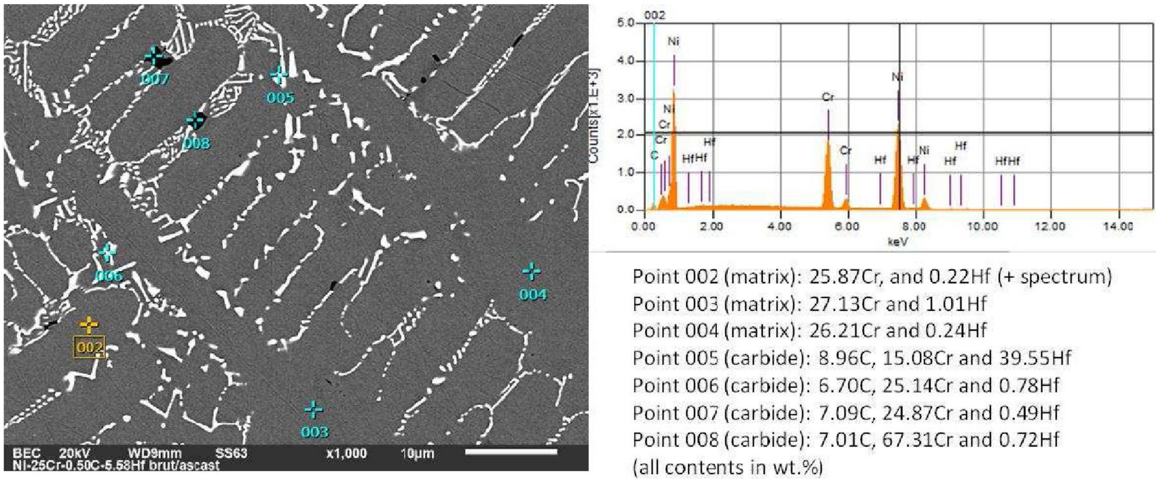
Point 002 (matrix): 26.04Cr ;
Hf: not detectable (+ spectrum)
Point 003 (matrix): 27.27Cr and 1.01Hf
Point 004 (matrix): 25.79Cr and 0.52Hf
Point 005 (carbide): 6.07C, 24.11Cr and4.79Hf
Point 006 (carbide): 6.19C, 25.30Cr and 0.42Hf
(all contents in wt.%)

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



Point 002 (matrix): 25.21Cr, and 0.20Hf (+ spectrum)
Point 003 (matrix): 25.91Cr and 0.07Hf
Point 004 (matrix): 25.69Cr and 0.37Hf
Point 005 (carbide): 12.92C, 35.18Cr and 23.86Hf
Point 006 (carbide): 6.25C, 24.04Cr and 0.19Hf
Point 007 (carbide): 5.64C, 24.42Cr and 0.61Hf
Point 008 (carbide): 6.37C, 23.38Cr and 0.21Hf
(all contents in wt.%)

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



Point 002 (matrix): 25.87Cr, and 0.22Hf (+ spectrum)
Point 003 (matrix): 27.13Cr and 1.01Hf
Point 004 (matrix): 26.21Cr and 0.24Hf
Point 005 (carbide): 8.96C, 15.08Cr and 39.55Hf
Point 006 (carbide): 6.70C, 25.14Cr and 0.78Hf
Point 007 (carbide): 7.09C, 24.87Cr and 0.49Hf
Point 008 (carbide): 7.01C, 67.31Cr and 0.72Hf
(all contents in wt.%)

Figure 7 : Ni-25Cr-0.50C-5.58Hf alloy: locations of the pinpoint EDS measurements and the results obtained (Ni: rest).

General commentaries

Obviously, the addition of hafnium in sufficiently great amounts to promote the formation of HfC carbides instead of chromium carbides was successfully: the chromium carbides were totally replaced by hafnium carbides for the two alloys in which Hf atoms were about in the same number as the C atoms, while HfC formed preferentially to chromium carbides when there were more C atoms than Hf atoms (case of the Ni-25Cr-0.50C-3.72Hf alloy). Since the hafnium content in the matrix seemed to be very low (even negligible) it appeared that the Hf atoms tend to be wholly involved in the formation of MC carbides. This was earlier not the case for tantalum in nickel-based alloys[13] for which the chromium carbides were in contrast favored by comparison to TaC carbides in a similar chromium-rich nickel base.

This substitution of chromium carbides by hafnium carbides seemingly led to an increase in hardness (and maybe in mechanical properties at room temperature as well as at high temperature). This can be due to the higher intrinsic Vickers hardness of HfC carbides (2913) by comparison to the chromium carbides ones (1650 for $Cr_{23}C_6$ and 1336 for Cr_7C_3)[14], but also to the apparently slightly higher volume fractions of HfC by comparison to the chromium carbides ones in the ternary alloys with the same carbon contents.

CONCLUSIONS

Thus, a significant interdendritic carbide network of HfC can exist in the microstructures of chromium-rich nickel alloys to mechanically reinforce them, in contrast with what was earlier observed with tantalum and TaC carbides in nickel-based alloys with neighbour chemical compositions. This first led here to an increase in hardness for same carbon contents.

This exploration of the possibility of presence of HfC carbides in refractory metallic alloys rich in chromium will be continued in a further work, this time dealing with cobalt-based alloys[15].

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