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Equiaxed Cast Polycrystalline Refractory Alloys Designed to Be Strengthened by Mono-carbides: Dependence of the As-Cast Microstructure on the Base Element and on the MC-former Element

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Abstract:

This work consists in a general exploration of the microstructures which can be obtained after solidification for a wide series of alloys for which the base element and the MC-former element both vary. For given contents in Cr, M and C contents, the compositions of nineteen alloys were considered. They are based on Ni, Co, Fe or Nb while the wished carbides are TiC, TaC, NbC, HfC or ZrC. After solidification and cooling, metallographic samples were prepared and characterized by electron microscopy to discover the obtained microstructures. Results show first that MC carbides are generally successfully obtained at the expense of other possible carbides (e.g. all Co-based alloys) but there also are several exceptions (e.g. some Ni-based alloys). Second, the obtained MC-carbides are on a eutectic origin and script-like shaped but here too some exceptions may be noted (e.g. HfC in Nb-based alloys). Globally the results of this work demonstrate that the principle of dendritic matrix associated to MC carbides with a script-like morphology is not systematically obtained: the nature of (base element, MC-former element) governs the as-cast microstructures of the alloys for these particular Cr and C compositions and may lead to other carbides and even other microstructures types.

Keywords: Solidified refractory alloys; Monocarbides; As-cast microstructures; Base element; MC-former elements

Introduction

Superalloys are used since several decades in industry aeronautics, power generation and industries involving processes working at elevated temperature [1]. Till today their usage became more and more expanded because of the energy efficiency demand increase [2]. The first superalloys were issued from classical foundry processes [3] but new ways of elaboration of these high performance refractory metallic materials appeared more (e.g. Powder Metallurgy [4,5], single crystalline solidification [6,7]) or less (additive manufacturing [8,9]) long ago. Although that the elaboration principle is rather old [10, 11] foundry processes leading to polycrystalline equiaxed microstructures still possess interesting potential for obtaining high performance superalloys for elevated temperature applications. Indeed, some chemical compositions and the following microstructures allow very high melting start temperature ($T \geq 1300^\circ\text{C}$), high strength of matrix (austenitic and dendritic), sufficient matrix hardening (solid solution strengthening and/or precipitation strengthening) and hard particles taking care of the interdendritic cohesion (such as script-like eutectic carbides). An emblematic example is the one of an equiaxed chromium-containing cobalt-based alloy with a dendritic matrix and an interdendritic carbide network closely imbricated with the periphery of the dendrites. Such an alloy owns a continuous polycrystalline compact austenitic matrix with high hardness and intrinsic resistance, able to deliver chromium to combat hot corrosion, and the cohesion of which is given by the script-like TaC carbides interlocking each dendrite with its neighbors. The commercial Mar-M 509 superalloy corresponds globally to this description [1,11] despite the presence of chromium carbides together with the TaC. Another industrial alloy [12], despite the additional presence of nickel, better matches this microstructural principle which led to remarkable performances at elevated temperatures under stresses and chemical aggressiveness.

TaC carbides were successfully obtained as the single carbide present in the later alloy thanks to a good atomic correspondence between C and Ta and the high thermodynamic stability of TaC in a cobalt-chromium environment. It is logical to imagine that this %_{at} M=%_{at} C condition may led to the same results in other bases, for example involving nickel, iron... and in the case of other MC-former elements such as Ti or Nb for example. To check this, a study was initiated for several combinations M – M', with the M base element being Co, Ni Fe and Nb and the M' monocarbide-former element being Ti, Ta, Nb, Hf or Zr. A series of about twenty different alloys were thus elaborated and their as-cast microstructures characterized, hoping that all will look like the specimen shown in Figure 1. The purpose of this article is to present the obtained as-cast microstructures.

Methodology

Elaboration of the alloys

All the alloys were wished issued from the mixing of initially pure elements. Thus, small parts of pure Co, Ni, Fe, Nb, Cr, C (graphite), Ti, Ta, Hf and Zr (purity > 99.9 wt.%, graphite: 100%) were bought by Alfa Aesar and Aldrich. They were weighed using a precision balance to obtain final charges with the following requirements:

Cr: between 25 and 35 wt.%

C: between 0.4 and 0.5 wt.%

Ti, Ta, Nb, Hf and Zr: weight percent chosen to have the same molar content as carbon (globally Ti: near 2 wt.%, Ta and Hf: near 7.5 wt.%, Nb: near 4 wt.%, Zr near 3 wt.%)

Co, Ni, Fe and Nb (if base element): balance

Masses to melt: 40g for the Ni-based, Co-based and Fe-based alloys; 10g for the Nb-based alloys

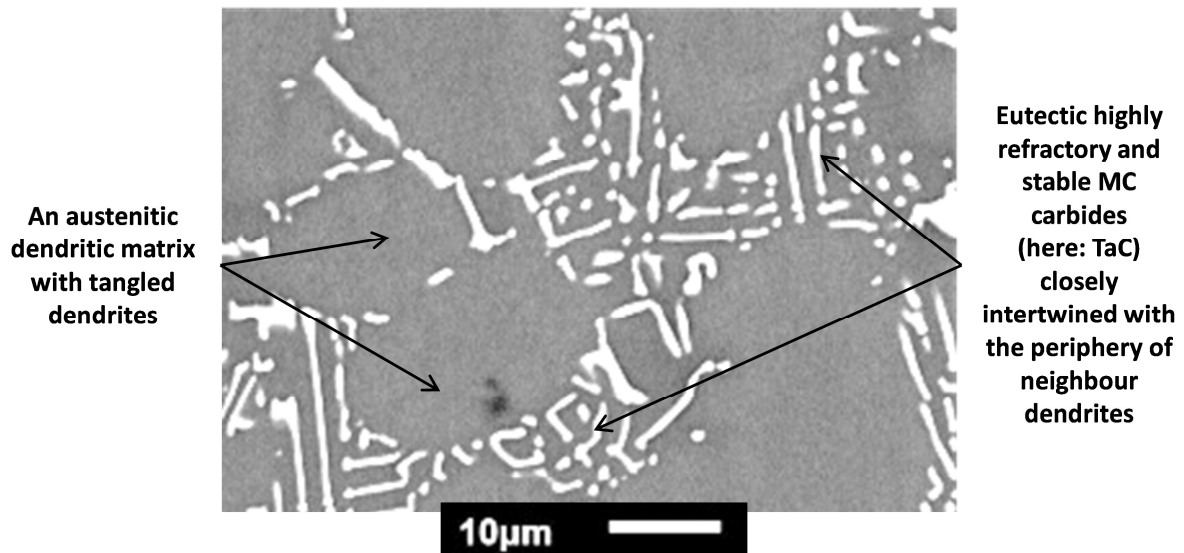


Figure 1. Microstructure of a Co(bal.)-25Cr-0.5C-7.5Ta alloy; the wished characteristics for high mechanical resistance at elevated temperature

The mixed elements corresponding to a final alloy were all placed together in the crucible of a high frequency induction furnace (CELES, France; power: 50kW). This crucible is metallic, made of copper, and it was continuously cooled by circulating water at ambient temperature during the elaboration steps.

After having laid down the pure elements, a silica tube was placed around the crucible and closed to allow the evacuation of the present air, by pumping it. The crucible and silica tube were surrounded by a water-cooled copper coil through which an alternative current will circulate (frequency: between 100 and 150 kHz, voltage: between 4 and 5kV, depending on the alloy). After three-times pumping until 5×10^{-5} atm followed by filling by pure Argon, the inside atmosphere of pure Ar was rated at about 400 mbars.

Heating led to the melting of the charges made of pure elements and the obtained liquid alloy was maintained at the highest reached temperature during several minutes to achieve total chemical homogeneity. During the cooling, operated by decreasing the input power/voltage, the alloys started solidify, and later cooled in solid state. After about 20 to 30 minutes after the end of isothermal stage in the liquid state, the obtained ingots were again at room temperature and ready to be extracted from the crucible.

The successive steps of the elaboration are illustrated by the three photographs presented in Figure 2 while an example of obtained ingot is shown in Figure 3.

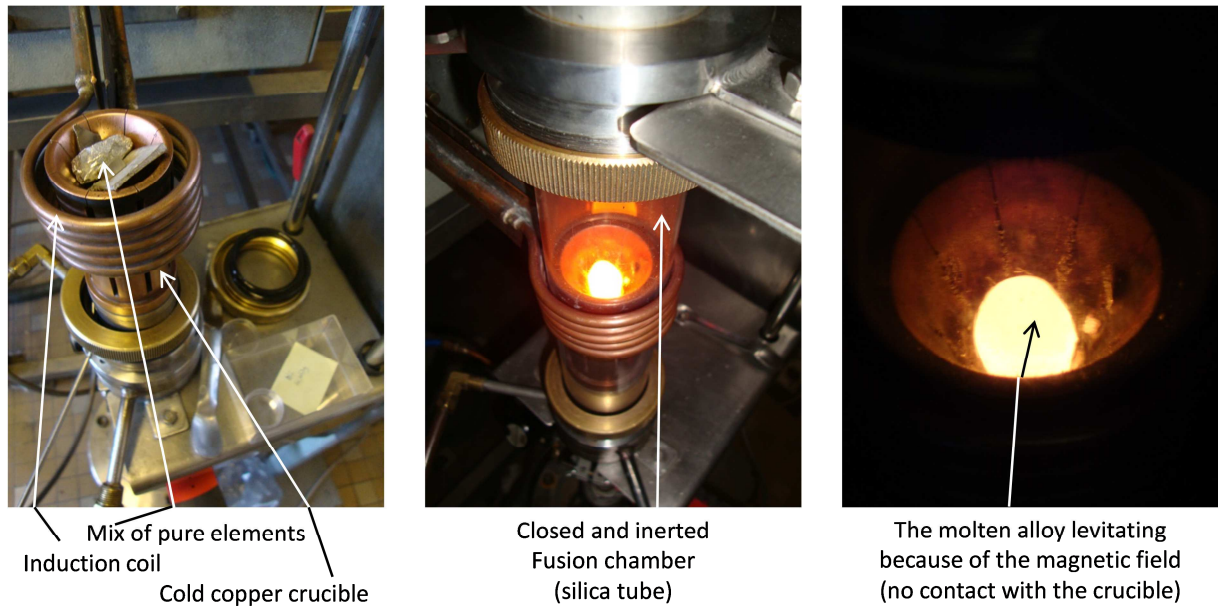


Figure 2. Illustration of the melting and solidification of the alloys by high frequency induction heating under inert atmosphere



Figure 3: Macrophotographs of one of the obtained ingots (two different views)

Metallographic characterization and hardness measurements

Each ingot was first cut using a metallographic saw. This allowed extracting a part of alloy which was embedded in a cold resin + hardener mixture (ESCIL, France). After total stiffening of the embedding resin the obtained samples were extracted from their plastic molds and ground. Grinding started by using #120 or #240-grade SiC papers and finished by

#1200 or #2400-grade ones. After ultrasonic cleaning polishing was carried out using a textile disk enriched with 1 μm hard particles.

The obtained mirror-like samples were put one by one in the chamber of a Scanning Electron Microscope, model JSM-6010LA (JEOL, Japan). Their microstructures were observed in Back Scattered Electrons mode (acceleration voltage: 20kV), at different magnification ratings. Energy Dispersive Spectrometry was used to control the obtained chemical compositions by full frame analysis. Additionally, spot analyses were performed on the seen particles to try identifying them and to know the chemical composition of the matrix. X-ray diffraction was also carried out for the most of the studied alloys. This was done using a Philips X-Pert Pro diffractometer.

The metallographic samples were also subjected to indentation tests to assess the hardness of all alloys. This was carried out using a Testwell Wolpert indentation machine, according to the Vickers method. The applied loads were adjusted to the apparent hardness of the alloys: 10kg for the less hard ones and 30kg for the hardest ones. In the cases where possible fracture may happen because of critical lack of toughness 10kg was preferred at the expense of 30kg for some of the hardest alloys.

Results

Machinability and hardness

The first observation concerns the cutting of the ingots. Cutting was rather easy for the Ni-based and Fe-based alloys and more difficult for the cobalt-based alloys. The most serious difficulties of cutting were encountered for the Nb-alloys: long time of cutting although the size of these ingots were smaller than for the other alloys, significant heating of both ingot and cutting tool... This was in obvious relation with hardness. The indentation tests showed that, independently on the type of carbide present, this is the matrix nature which governs the room temperature hardness of these alloys: around 200 Hv for all the Ni-based alloys and Fe-based alloys, around 350 Hv for all the cobalt-based alloys, and around 900 Hv for all the Nb-based alloys. These three levels of hardness globally correspond to the three levels of cutting difficulty.

Results of X-ray diffraction runs and of the global composition EDS measurements

The obtained XRD spectra gave essentially knowledge about the matrixes of the alloys. All the ones of the nickel-based alloys are Face Centered Cubic (FCC), the ones of the cobalt-based ones are composed of a mix of FCC part and of a Hexagonal Compact part. The matrixes of the iron-based alloys were all ferritic (Body Centered Cubic, BCC). The niobium-base alloys all contain a Nb-based BCC phase and a Cr_2Nb phase with two crystalline structures: BCC and Hexagonal. In contrast, no diffraction peaks corresponding to the carbides supposed to be present were detected, probably because their volume fraction probably not great enough. The full frame Energy Dispersion Spectrometry analyses allowed to verify that the targeted chemical compositions of alloys were all well respected. However, this concerns only the elements heavy enough, as is to say all of them except carbon.

Some examples of as-cast microstructures containing MC as single carbides present

The observations carried out in electron microscopy demonstrate that obtaining the initially wished carbides was not successful in all cases. Before having a look to all the obtained microstructures one can choose some of them to preliminarily illustrate what is called a success and what can be considered as a failure. Two satisfying microstructures are presented in Figure 4.

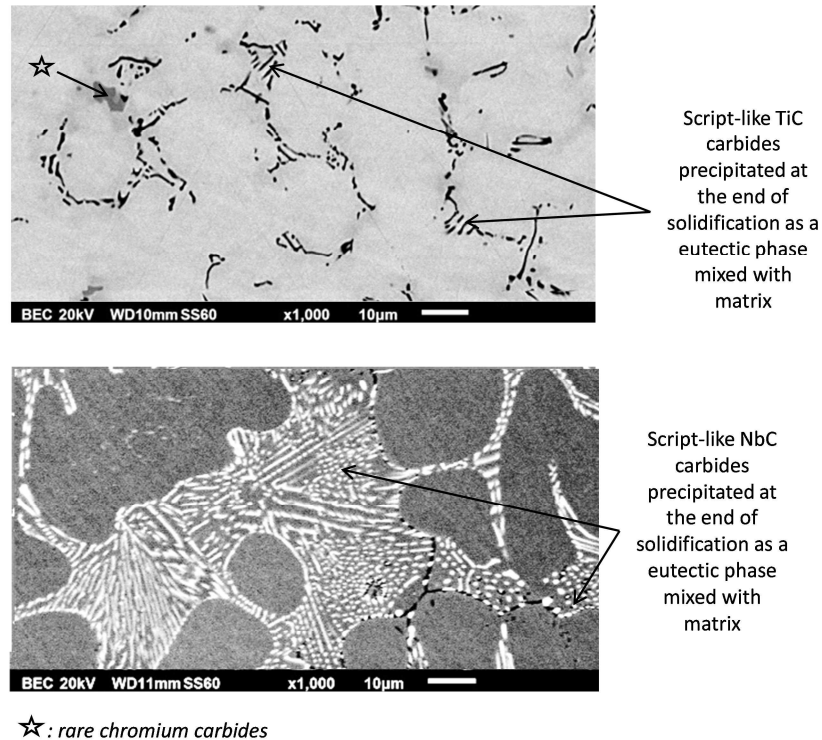


Figure 4. Two examples of successful obtaining of MC carbides as (almost) single carbide present (top: Co-25Cr-0.5C-2Ti, bottom: Fe-25Cr-0.5C-3.9Nb)

The top micrograph is the one of the Co-25Cr-0.5C-2Ti. The microstructure of this alloy is made of a dendritic matrix and interdendritic carbides. The matrix is compact, with a crystalline structure combining a FCC one and a HCP one, the first one being inherited from the solidification and the high temperature part of cooling and the second one resulting to a not totally achieved FCC → HCP allotropic transformation during the last part of cooling. This particular composition was revealed only by XRD diffractograms since the chemical and compactness homogeneities did not allow obtaining contrast for images taken in the BSE mode. During heating to service temperature the HCP structure will disappear, this leading to a matrix totally austenitic, particularly interesting for its intrinsic strength combined with a good hot ductility and toughness. Concerning the carbides present, despite the existence of some rare and small chromium carbides, the carbide population is composed of script-like carbides located in the interdendritic boundaries where they are interlocked with the periphery of the dendrites of matrix. Unfortunately, after the failure of XRD for their clear identification because a too low surface fraction of the emerging carbides, spot EDS analyses did not allow themselves specifying that they are TiC carbides but one can however consider that this is the

case since these spot analyse revealed that these particles contain high concentrations of Ti and C.

The bottom micrograph shows the case of the Fe-25Cr-0.5C-3.9Nb. TaC carbides, identified by spot EDS analysis (showing high concentration in Ta and C simultaneously), were obtained. As the TiC carbides mentioned just above they are script-like shaped and located between neighbor dendrites with the periphery of which they are imbricated. The matrix is BCC, as demonstrated by XRD. Some small rare chromium carbides are also present here and there but, as for the previous alloys, the part that they take in the total carbide population is extremely small.

Some examples of as-cast microstructures where MC carbides are less present or almost totally absent

There are also alloys the as-cast microstructures of which do not correspond to the wished criteria. Two examples are shown in Figure 5. The top micrograph illustrates the microstructure obtained for the Ni-25Cr-0.5C-2Ti composition. Although its microstructure looks like the wished ones with its dendritic austenitic matrix and its interdendritic carbides obviously forming a eutectic compound with the outermost part of the matrix dendrites, these carbides are not MC carbides but chromium carbides. This is revealed first by their acicular shape instead a script-like one, and second by spot analysis which showed high concentration in C and Cr and absence of Ti.

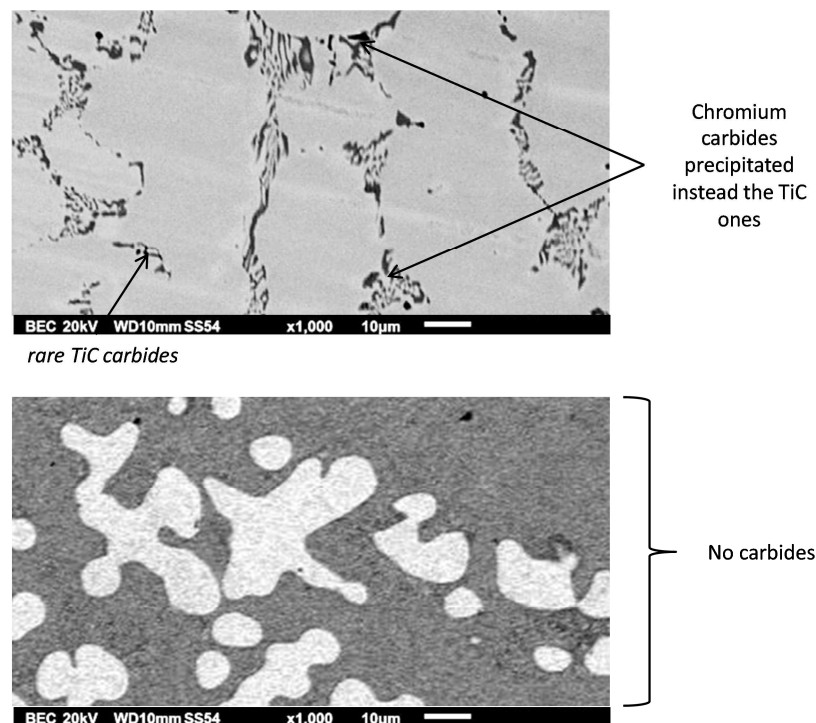


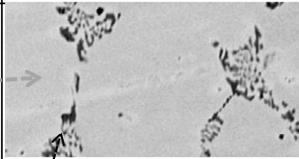
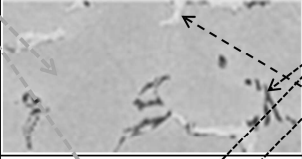
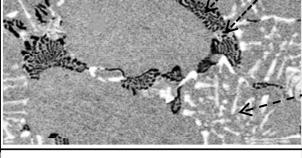
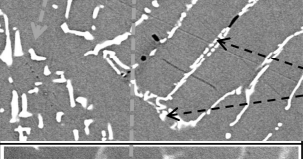
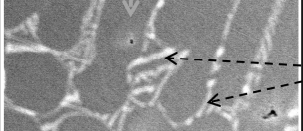

Figure 5. Two examples of no obtaining of any MC carbides (top: Ni-25Cr-0.5C-2Ti, bottom: Nb-33Cr-0.4C-2.9Zr)

The as-cast microstructure of one of the niobium alloys is given in the bottom micrograph, the Nb-33Cr-0.4C-2.9Zr one. Its microstructure is composed of dendrites of a BCC niobium-based phase (XRD, EDS) and of a eutectic mix of this bright Nb-phase and a dark Cr₂Nb one. Absolutely no MC carbides were present. The Cr₂Nb Laves phase may be of two crystalline structures, BCC and hexagonal. Some very small black particles (isolated carbides?) also exist here and there but EDS was unable to characterize them because their extremely low sizes.

General report for the Ni-based alloys

The metallographic results obtained for the as-cast state of the five nickel-based alloys are compiled in Table 1. Two successful MC formations were observed (left column): HfC in the Ni-25Cr-0.5C-5.6Hf alloy, and ZrC in the Ni-25Cr-0.5C-3.8Zr one. In both cases these carbides are the single carbide present, with the required location and morphology. Other MC carbides were also obtained in two other cases but not as the single carbide phase present (central column): TaC (respectively NbC) get along with chromium carbides (dark/black carbides) in the Ni-25Cr-0.4C-6Ta (resp. Ni-25Cr-0.5C-3.9Nb) alloy. The last nickel-based alloy (right column) does not contain any MC carbides but only chromium carbides. No TiC carbide precipitated during the solidification of this alloy.

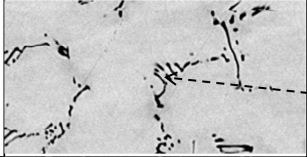


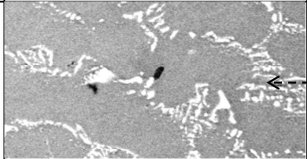
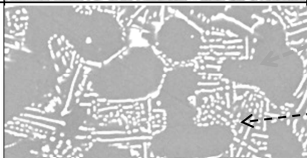
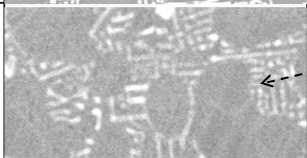
Table 1. Microstructural results (MC obtained or not?) for the Ni-based alloys with the different MC-former elements; SEM/BSE micrographs

NICKEL-BASED ALLOYS			
MC-type (alloy)	Only MC	MC & Cr carbides	Only Cr carbides
TiC ? <u>Alloy (cont. in wt.%):</u> Ni(bal.)-25Cr-0.5C-2Ti	dendritic matrix		
TaC ? <u>Alloy (cont. in wt.%):</u> Ni(bal.)-25Cr-0.4C-6Ta			eutectic chromium carbides eutectic TaC
NbC ? <u>Alloy (cont. in wt.%):</u> Ni(bal.)-25Cr-0.5C-3.9Nb			eutectic NbC
HfC ? <u>Alloy (cont. in wt.%):</u> Ni(bal.)-25Cr-0.5C-5.6Hf		eutectic HfC	
ZrC ? <u>Alloy (cont. in wt.%):</u> Ni(bal.)-25Cr-0.5C-3.8Zr		eutectic ZrC	Scale bar for all micrographs:  25 μm

General report for the Co-based alloys

As proved by the information presented in Table 2, a cobalt-chromium base is particularly suitable to obtain MC carbides as single carbide phase present, with furthermore the wished morphologies and locations. Black script-like eutectic TiC carbide well precipitated during the solidification end of the Co-25Cr-0.5C-2Ti alloy. Similar results were obviously obtained for the bright TaC, NbC, HfC and ZrC carbides in the Co-25Cr-0.4C-7.5Ta, Co-25Cr-0.5C-3.9Nb, Co-25Cr-0.5-7.4Hf and Co-25Cr-0.5C-3.8Zr alloys, respectively. However one must note that some rare and small chromium carbides appeared in some cases while the origin of the obtained MC carbides was not exclusively eutectic for some of these alloys. Notably, the Co-25Cr-0.5C-7.4Hf, which is rich in script-like eutectic HfC carbides, also contains some dispersed blocky HfC carbides, not specifically located in the interdendritic spaces. The later ones can be suspected to have appeared at the early stage of solidification, as a pre-eutectic carbide phase.

Table 2. Microstructural results (MC obtained or not?) for the Co-based alloys with the different MC-former elements; SEM/BSE micrographs

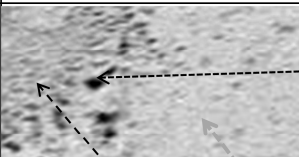
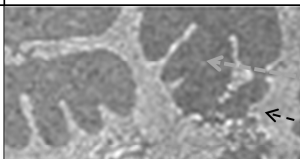
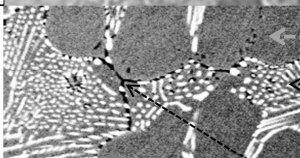
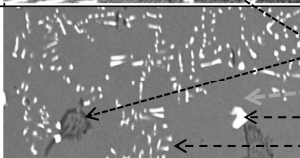
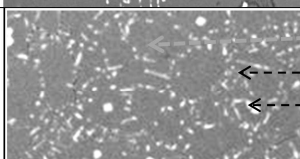

COBALT-BASED ALLOYS			
MC-type (alloy)	Only MC	MC & Cr carbides	Only Cr carbides
TiC ? <u>Alloy (cont. in wt.%):</u> Co(bal.)-25Cr-0.5C-2Ti		eutectic TiC	dendritic matrix Scale bar for all micrographs:  25 μm
TaC ? <u>Alloy (cont. in wt.%):</u> Co(bal.)-25Cr-0.4C-7.5Ta		eutectic TaC	
NbC ? <u>Alloy (cont. in wt.%):</u> Co(bal.)-25Cr-0.5C-3.9Nb		eutectic NbC	
HfC ? <u>Alloy (cont. in wt.%):</u> Co(bal.)-25Cr-0.5C-7.4Hf		eutectic HfC	
ZrC ? <u>Alloy (cont. in wt.%):</u> Co(bal.)-25Cr-0.5C-3.8Zr		eutectic ZrC	

General report for the Fe-based alloys

This is the role of Table 3 to summarize the observation results concerning the iron-based alloys. Obtaining MC carbides in their as-cast microstructures was generally successful but not as systematic as for the cobalt-based alloys. First TiC carbides were not the single

carbide present in the Fe-25Cr-0.5C-2Ti alloy since many chromium carbides appeared too (middle column). For the alloys containing exclusively – or at least mainly – MC carbides, the script-like shape was really obtained only for the Fe-30Cr-0.4C-6Ta alloy (eutectic TaC) and for the Fe-25Cr-0.5C-3.9Nb alloy (NbC). The HfC and the ZrC obtained in the Fe-25Cr-0.5C-5.6Hf alloy and the Fe-25Cr-0.5C-3.8Zr one, respectively, are more discontinuous, made of elongated particles without apparent contact between them.

Table 3. Microstructural results (MC obtained or not?) for the Fe-based alloys with the different MC-former elements; SEM/BSE micrographs

IRON-BASED ALLOYS			
MC-type (alloy)	Only MC	MC & Cr carbides	Only Cr carbides
TiC ? <u>Alloy (cont. in wt.%):</u> Fe(bal.)-25Cr-0.5C-2Ti			chromium carbides
TaC ? <u>Alloy (cont. in wt.%):</u> Fe(bal.)-30Cr-0.4C-6Ta		TiC eutectic TaC	dendritic matrix
NbC ? <u>Alloy (cont. in wt.%):</u> Fe(bal.)-25Cr-0.5C-3.9Nb		eutectic NbC	
HfC ? <u>Alloy (cont. in wt.%):</u> Fe(bal.)-25Cr-0.5C-5.6Hf		chromium carbides pre-eutectic HfC eutectic HfC	
ZrC ? <u>Alloy (cont. in wt.%):</u> Fe(bal.)-25Cr-0.5C-3.8Zr		pre-eutectic ZrC eutectic ZrC	Scale bar for all micrographs:  25 μm

General report for the Nb-based alloys

As clearly demonstrated by Table 4, the niobium-based alloys behaved totally differently to the previous alloys families. The microstructures of three of them (Nb-33Cr-0.4C-1.6Ti, Nb-30Cr-0.4C-5.9Ta and Nb-33Cr-0.4C-2.9Zr) are characterized by the presence of dendrites of BCC Nb-based matrix and of a seemingly eutectic interdendritic compound made of BCC Nb-phase and Cr₂Nb Laves phase. No carbides seem existing in these alloys but the presence of some rare black particles must be noticed even if it is impossible to specify them taking into account their extremely small size. The Nb-33Cr-0.4C-5.8Hf seems a little different from these three alloys since it contains less pre-eutectic BCC Nb-phase (which is maybe no dendritic) and more {BCC Nb-phase & Cr₂Nb}–made eutectic compound. MC carbides are obviously present in this later alloy, but with totally different morphology and

location if compared to the alloys of the three other families. Here HfC are round and small, and seem systematically attached to the Nb-phase globules, or inside them.

Table 4. Microstructural results (MC obtained or not?) for the Nb-based alloys with the different MC-former elements; SEM/BSE micrographs

NIObIUM-BASED ALLOYS			
MC-type (alloy)	Major phases ↓	existing phases ↓	(almost) no carbides!
TiC ? <u>Alloy (cont. in wt.%):</u> Nb(bal.)-33Cr-0.4C-1.6Ti	In all alloys: Back Centered Cubic Nb-based solid solution (the pale one)	Cr₂Nb intermetallic	
TaC ? <u>Alloy (cont. in wt.%):</u> Nb(bal.)-30Cr-0.4C-5.9Ta		and	
HfC ? <u>Alloy (cont. in wt.%):</u> Nb(bal.)-33Cr-0.4C-5.8Hf	both Cubic and Hexagonal Cr ₂ Nb phases	(Nb, Hf)C	
ZrC ? <u>Alloy (cont. in wt.%):</u> Nb(bal.)-33Cr-0.4C-2.9Zr	Scale bar for all micrographs: 25 μm	Cr₂Nb intermetallic	

Discussion

MC are among the most thermodynamically stable carbides [13]. They are known to precipitate at solidification or during solid state isothermal stages at high temperature in some superalloys containing MC-former elements and carbon with adequate contents, at the expense of other types of possible carbides. For instance, the presence of C in atomic excess by comparison with Ta leads to significant precipitation of eutectic TaC in the cast cobalt-based Mar-M 509 superalloy [1], while another cobalt-based superalloy used in industry [12] is strengthened by an interdendritic carbide network made of TaC exclusively thanks to the atomic equivalence between Ta and C in its chemical composition. The predominance of different MC carbides by the same choice of M and C atomic contents was rather recently explored in the case of cobalt-chromium alloys [14]. This allowed verifying that MC carbides form at the expense of all other types of carbides in such base.

This result was found again here with the five studied chromium-containing alloys based on cobalt. However one can see with the present work that results are much more contrasted with the three other alloys systems: the iron-chromium alloys effectively contain principally MC carbides when M is Ta, Nb, Hf or Zr, but with morphologies more or less similar to the TaC ones in cobalt-chromium alloys and it is not sure that the resulting of mechanical strengthening at high temperature can be of a so good level (notably for a ferritic structure of matrix. TiC, TaC and NbC meet the concurrence of chromium carbides in nickel-chromium carbides, with as result a co-existence of MC and Cr_xC_y in the microstructure, and

even a total absence of MC (case of Ti). In such case the M element stays with rather high content in solid solution in the matrix, and even all the M atoms can be stocked in the matrix when no MC formed: this was verified here, for example for Ti in the nickel-chromium alloy by EDS spot analyses. Even when MC formed as single carbide for a chemical composition designed to respect the molar equivalence between M and C, a significant part of M may be present in solid solution in the matrix. This was the case here for instance for tantalum in the Co-25Cr-0.5C-7.4Ta in which the matrix contained almost 2 wt.% of the 7.4wt.% of Ta of the alloy. In this later case carbon atoms were automatically present in solid solution in the matrix of this alloy. In contrast, Hf was never present in solid solution in the matrix of the alloys, regardless of the base element among Ni, Co and Fe. In contrast, as for Ta, Ti and Zr, Hf was present in significant quantity (several wt.%) in the Nb-phase and in the Cr₂Nb phase.

If cobalt played here a particular role by allowing the systematic formation of the wished MC carbides exclusively, hafnium acted itself as a constant MC-former element since it was always present in the alloys of this work containing Hf. The molar equivalence of Hf and C led to the formation of carbides made of exclusively HfC in the Ni-based, Co-based and Fe-based alloys, while HfC was the only MC carbide to form with a visible presence in niobium-chromium alloys. Unfortunately no strengthening effect can be awaited from these small and round HfC particles formed in this Nb-33Cr-0.4C-5.8Hf alloy for high temperature uses.

Conclusion

The formation of MC carbides during the solidification of M-{25 to 35}Cr-{0.4 to 0.5}C-M' alloys (M': monocarbide-former element) is thus obviously more complex than the previous observations – limited to cobalt-chromium systems – allowed to think. Chromium carbides may be unexpectedly thermodynamically favored in some cases and when MC successfully forms, this is not necessarily with the morphology the most favorable to high mechanical resistance at elevated temperature. The potentially best combinations for such objective are nickel-chromium with HfC and cobalt-chromium with any of the MC considered here. Although being an alloy system globally favorable to MC formation iron-chromium alloys risk to be handicapped by the intrinsic weakness of the ferritic structure of their matrixes. Regarding the niobium alloys, this is more the lack of ductility and of toughness which would obstruct their use rather than the failure of precipitation of MC carbides during solidification.

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