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ARTICLE

Influence of the M and M' Metals on the Carbides Population in As-Cast M'-based Alloys Designed to be MC-Strengthened

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ABSTRACT

High temperature applications such as turbine blades for aeronautics or molten glass-shaping tools require the use of refractory metallic materials. Among the later ones, cast superalloys based on some transition metals and reinforced by MC carbides stay in good place and their metallurgy merits to be well known. This work consists in a general exploration of the as-cast microstructures which can be obtained after solidification and solid state cooling down to ambient temperature for a wide series of alloys for which the base element and the MC-former element both vary. For fixed contents in chromium and carbon contents, the compositions of a total of nineteen alloys were considered. These alloys are based on Ni, Co, Fe or Nb and the M content was each time chosen to favor the appearance of TiC, TaC, NbC, HfC or ZrC, as single carbide in a given alloy. After elaboration, metallographic samples were observed by electron microscopy to investigate the obtained microstructures. The obtained results show first that the MC carbides were in many cases successfully obtained at the expense of other possible carbides (for all Co-based alloys for example) but there are also several exceptions (notably for some Ni-based alloys). Second, the obtained monocarbides have a eutectic origin and they are script-liked shaped. However they are here too some exceptions, as the rare HfC obtained in a Nb-base). In general, the results obtained in this work show that the principle of dendritic matrix combined with MC carbides with a script-like morphology is not necessarily obtained: the nature of the {base element, MC-former element} combination governs the microstructure of the alloy in its as-cast state for these particular compositions in chromium and carbon. In some cases other carbides may appear and the microstructures may be even of another type.

1. Introduction

Superalloys are used since several decades in industry aeronautics (notably as turbine disks and blades), power generation (such as burners and hottest parts of turbines) and industries involving processes working at elevated temperature (e.g. tools for shaping molten glasses) [1]. During the past decades their usage became more and more expanded because of the increase in efficiency demand [2]. The initial superalloys were elaborated by classical foundry processes [3] but new elaboration routes for these high performance refractory metallic materials appeared. These ones are more (Powder Metallurgy [4,5], single crystalline solidi-

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fication [6,7] …) or less (additive manufacturing [8,9] …) classic. Although their elaboration techniques are rather old [10, 11], foundry processes leading to polycrystalline and equiaxed microstructures still possess high interest for obtaining highly performant superalloys for applications at high temperature. Indeed, some chemical compositions and the resulting microstructures lead to very high melting start temperature (over 1300°C), high level of strength of the matrix (austenitic, dendritic), efficient strengthening of the matrix (solid solution and/or precipitation hardening) and strong particles useful for the interdendritic cohesion (e.g. script-like eutectic carbides). An important example may be given by an equiaxed chromium-containing cobalt-based alloy owning a dendritic matrix and taking benefit from interdendritic carbides closely imbricated with the periphery of the dendrites. Such an alloy possesses a continuous austenitic matrix with good hardness and high intrinsic mechanical resistance, moreover able to efficiently drive chromium toward the oxidation front to combat hot corrosion. Its interdendritic cohesion is favored by the script-like shape of the TaC carbides interlocking neighbor dendrites. The Mar-M 509 superalloy (commercial alloy from Martin-Marietta) globally corresponds to this description [1,11] despite the simultaneous presence of chromium carbides and TaC carbides (microstructure type similar to the one of the alloy showed in Figure 1). Another industrial alloy [12], despite the presence of nickel added to better stabilize the austenitic crystal structure of the matrix, corresponds more to this microstructural principle which led to remarkable performances at high temperatures under mechanical stresses and chemical aggressiveness.

The interest for MC carbides in alloys devoted for uses in severe conditions thus exists from several decades but this type of carbides is nowadays still considered for several types of alloys synthesized from various ways (sintering, solidification, coatings deposit…), ion cobalt-based [13, 14], iron-based [15], nickel-based [16, 17] and even High Entropy Alloys [18]. However alloy design involving MC carbides is rarely based on the exclusive presence of MC in the microstructure in which other carbides and other strengthening particles are present too. Obtaining in an alloy carbides which are only of the MC type is possible by correctly rating the contents in M and C. For instance tantalum monocarbides were successfully obtained as the single carbide present in one of the industrial alloys cited just above. This was successfully achieved thanks to both a good atomic correspondence between C and Ta and to the high thermodynamic stability of TaC in a cobalt-chromium environment. One can logically imagine that this $\{\%_{at}\,M=\%_{at}\,C\}$ condition may lead to the same results in other bases, for example involving nickel, iron… Other monocarbides-former elements such as Ti or Nb for example, which are stronger carbide-former elements than chromium [19], may be also considered. Thanks to their very high stability at elevated temperatures [20] one can expect exceptional high temperature properties in some cases, as this was already observed recently with the association of a polycrystalline dendritic Ni(Cr) matrix with eutectic HfC carbides: a matrix efficiently resisting hot oxidation/corrosion and morphologically highly stable script-like HfC interdendritic skeleton allowing high creep-resistance [21].

To check this, a study was initiated for several {M, M'} combinations, the M base element being Co, Ni Fe and Nb and the M' monocarbide-former element being Ti, Ta, Nb, Hf or Zr. Several recent results [22-25] were gathered and new alloy elaborations and microstructure characterizations were carried out to complete a collection based on 0.4-0.5 wt.%C and containing the corresponding M atomic contents for a molar {M=C} equivalence. A series of about twenty different alloys were thus obtained and taken into account in this study devoted to a metallurgical principle which is until today not yet recognized as competitor for g/g single crystalline superalloys despite its really great potential for applications gathering mechanically and chemically severe conditions of work for the used metallic pieces.

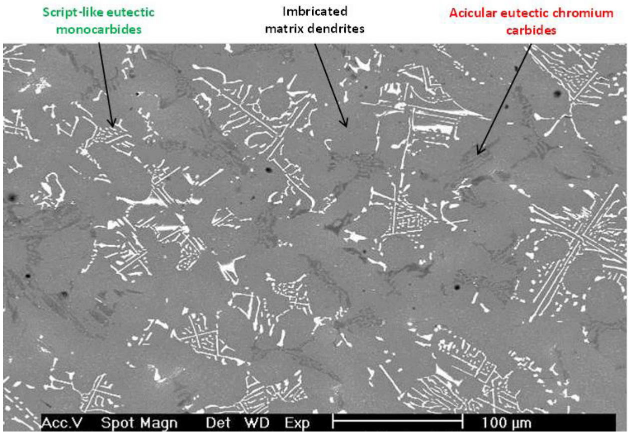

Figure 1. Microstructure of a Co(bal.)-9Ni-28Cr-1C-6Ta alloy

Note: It contains simultaneously some undesirable carbides (acicular eutectic chromium carbides) and the wished type of carbides: script-like eutectic MC carbides.

2. Methodology

2.1 Elaboration of the Alloys

All the alloys were issued from the mixing of initially

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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 provided by Alfa Aesar and Aldrich. They were weighed with accuracy to obtain final charges with the following contents:

(1) $25 \leq Cr \leq 35$ wt.% and $0.4 \leq C \leq 0.5$ wt.%

(2) Ti, Ta, Nb, Hf and Zr: weight fractions chosen to have the same molar content as C (approximately: Ti close to 2 wt.%, Ta and Hf each close to 7.5 wt.%, Nb close to 4 wt.%, Zr close to 3wt.%)

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

(4) Ingots masses: 40g for the Ni-based, Co-based and Fe-based alloys; 10g for the Nb-based alloys

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

After the introduction of the mix of 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 copper coil (water–cooled too) through which an alternative current will circulate. The frequency of this alternative current was between 100 and 150 kHz, and the applied voltage was between 4 and 5kV, this depending on the alloy. After 3 cycles made of pumping until 5×10^{-5} bars followed by filling by pure Argon, the inside obtained atmosphere was considered as being of pure Ar, with a pressure 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 solidifying, 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. They were then extracted from the crucible (Figure 2).

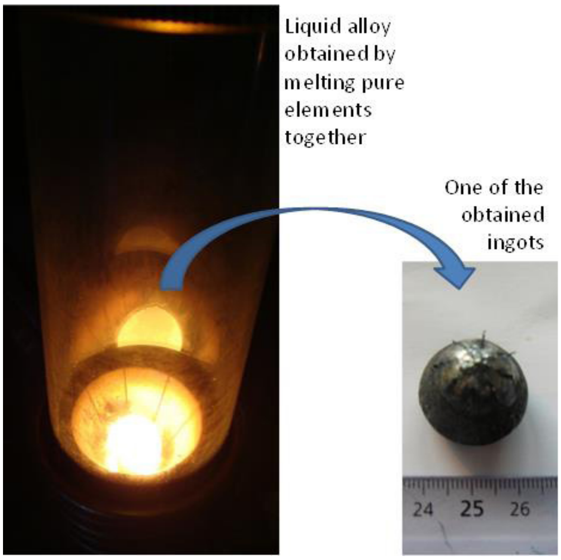

Figure 2. Illustration of the elaboration of the alloys for the study (high frequency induction melting and solidification in a cooled copper crucible)

2.2 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. They were ground by using first #120 or #240-grade SiC papers, then finished by #1200 or #2400-grade papers. 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 visible particles to try identifying them and to specify the chemical composition of the matrix. X-ray diffraction was also carried out for 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 crit-

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ical lack of toughness 10kg was preferred at the expense of 30kg for some of the hardest alloys.

3. Results

3.1 Machinability and Hardness

The first observation concerns the cutting of the ingots. Cutting was rather easy for the Ni-based and Fe-based alloys. In an opposite way this was more difficult for the cobalt-based alloys. The highest difficulties of cutting were met for the niobium-based alloys: long time of cutting although the size of these ingots were small, intensive heating of the ingot and the cutting tool… This was obviously in relation with hardness. The indentation tests showed that this is the matrix nature which governs the room temperature hardness of these alloys, more than the type of carbide. About 200 Hv was found for all the nickel-based alloys and iron-based alloys, against around 350 Hv for all the cobalt-based alloys, and around 900 Hv for all the niobium-based alloys. These three levels of hardness globally correspond to the three difficulty levels of cutting.

3.2 Results of X-ray Diffraction Runs and of the Global Composition EDS Measurements

The most often, the peaks really visible in the XRD diffractograms concern the matrixes of the alloys. All the nickel-based alloys own a Face Centered Cubic (FCC) matrix. The matrixes of the cobalt-based alloys are generally composed of a mix of a FCC part and of a Hexagonal Compact part. The ones of the iron-based alloys were all Body Centered Cubic, (BCC). Concerning the niobium-base alloys, they were composed of two major phases: a Nb-based BCC phase and a Cr_2Nb phase with two crystalline structures (BCC and Hexagonal). In contrast, the diffraction peaks corresponding to the carbides were very small by comparison with matrixes, because of their low volume fractions. If this was possible in some cases (e.g. cobalt-based alloys, Figure 3), this was sometimes impossible to specify the presence of some carbides by this way (e.g. niobium-based alloys, Figure 4).

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.

3.3 SEM/BSE Microstructure Observations for the Ni-based Alloys

The as-cast state microstructures of the five nickel-based alloys are illustrated in Figure 5. 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 (interdendritic) and morphology (script-like mixed with the periphery of the dendrites). Other MC carbides were also obtained in two other cases but not as the single carbide phase present: 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 (the one containing Ti) does not contain any TiC carbides but only chromium carbides.

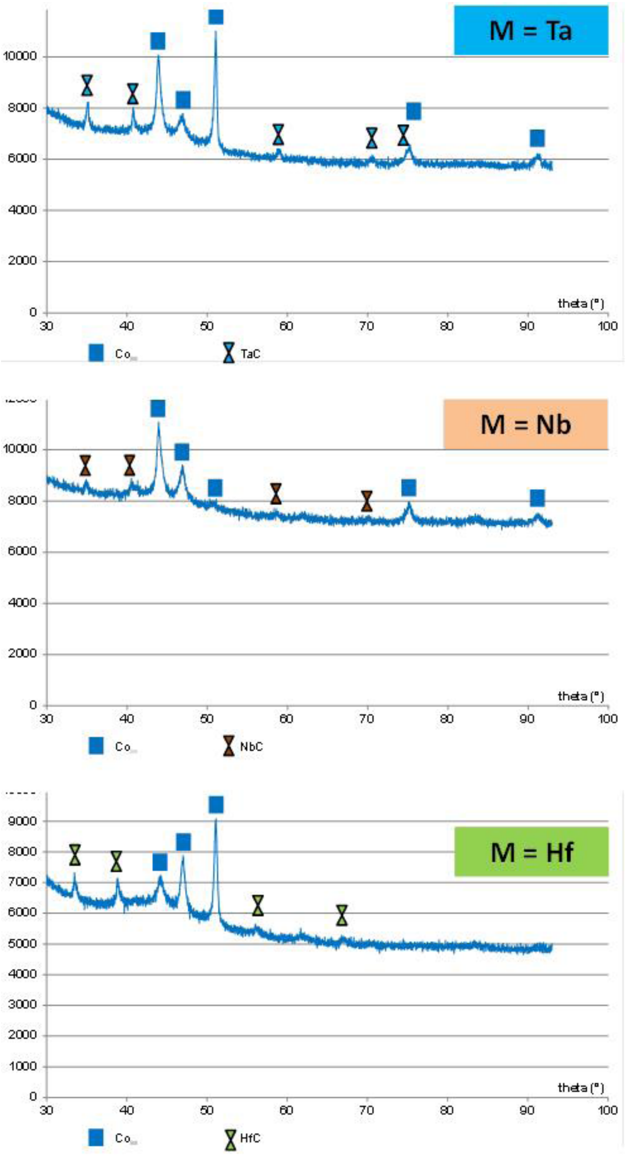

Figure 3. Three examples of XRD diffractograms allowing the identification of the carbides present (cobalt-based alloys with M=Ta (top), Nb (middle) and Hf (bottom) for forming MC carbides)

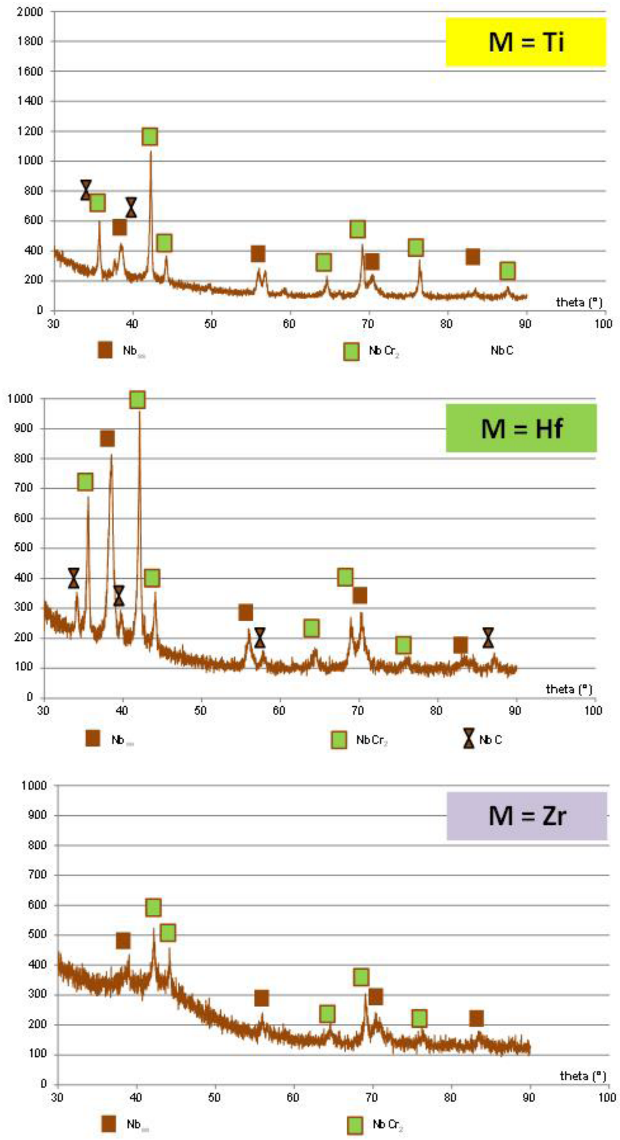

Figure 4. Three examples of XRD diffractograms from which the identification of the carbides present is not possible (niobium-based alloys with M=Ti (top), Hf (middle) and Zr (bottom) for forming MC carbides)

3.4 SEM/BSE Microstructure Observations for the Co-based Alloys

As illustrated by the micrographs presented in Figure 6, a cobalt-chromium base is particularly suitable to obtain MC carbides as single carbide phase present. In addition the wished morphologies and locations for the MC carbides were successfully obtained. 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 respectively 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. 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.

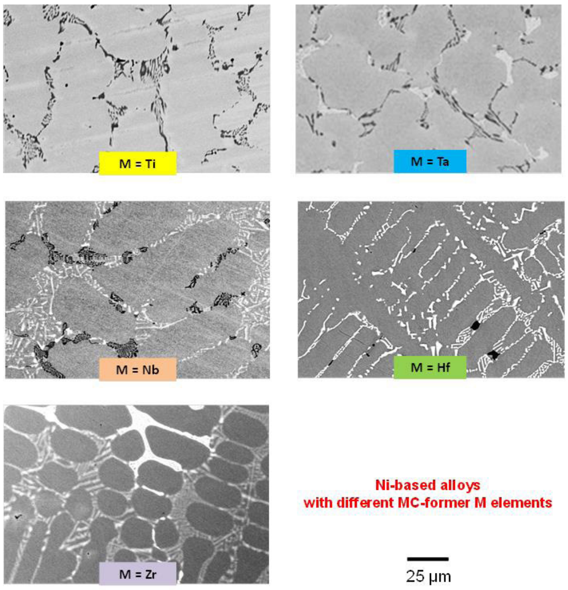

Figure 5. As-cast microstructures obtained for the Ni-based alloys with the different MC-former elements; SEM/BSE micrographs

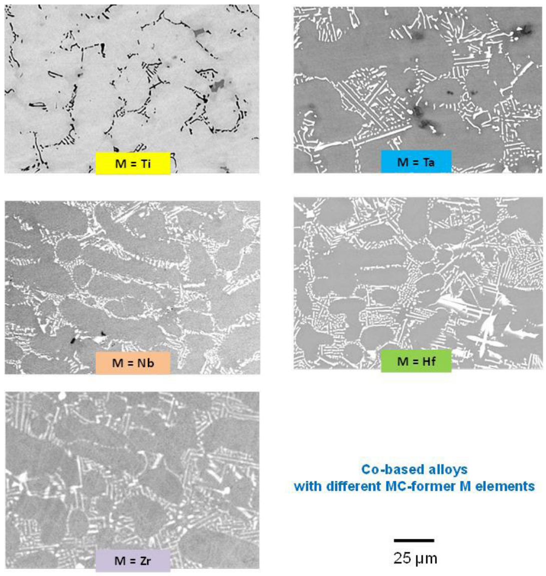

Figure 6. As-cast microstructures obtained for the Co-based alloys with the different MC-former elements; SEM/BSE micrographs

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3.5 SEM/BSE Microstructure Observations for the Fe-based Alloys

The as-cast microstructures of the iron-based alloys are presented in Figure 7. 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. 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. They are made of elongated particles without apparent contact between them.

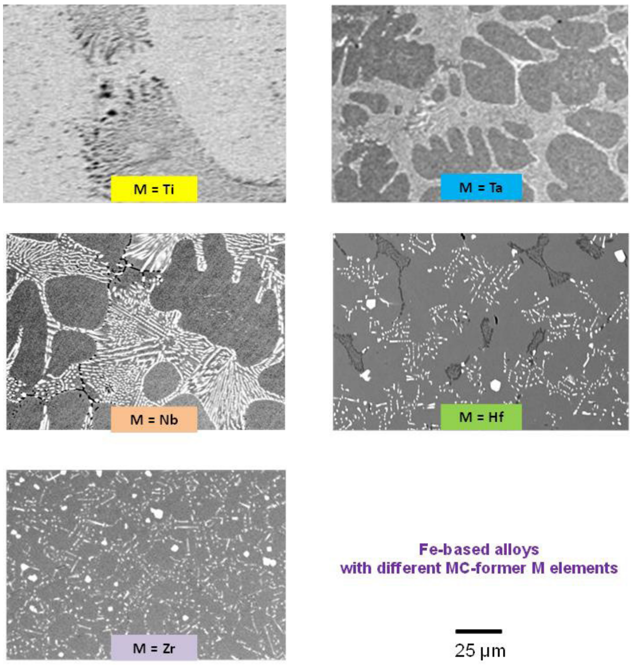

Figure 7. As-cast microstructures obtained for the Fe-based alloys with the different MC-former elements; SEM/BSE micrographs

3.6 SEM/BSE Microstructure Observations for the Nb-based Alloys

The niobium-based alloys behaved totally differently to the previous alloys families (Figure 8). 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 Cr_2Nb 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 alloy seems to be 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 & Cr_2Nb}–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.

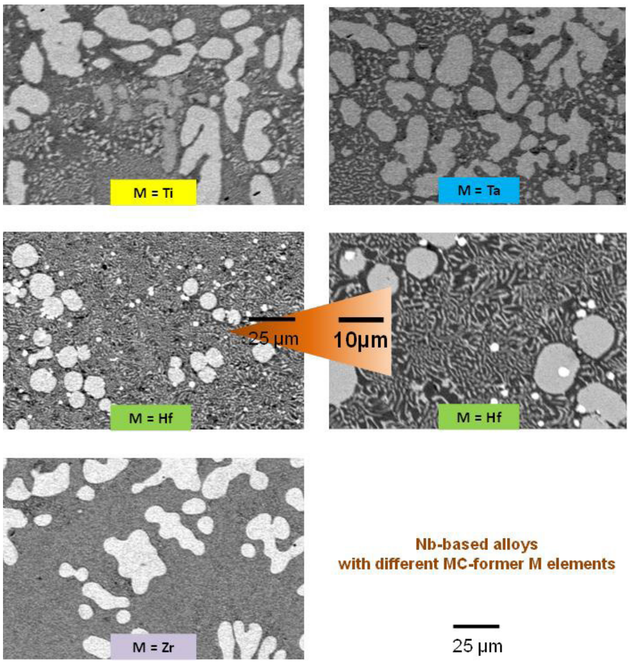

Figure 8. As-cast microstructures obtained for the Nb-based alloys with the different MC-former elements; SEM/BSE micrographs

4. Discussion

MC are among the most thermodynamically stable carbides [19]. 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 exclusively TaC 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

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of cobalt-chromium alloys [20]. 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 not strictly similar to the TaC ones (i.e. script-like) in cobalt-chromium alloys. It is not sure that the resulting of mechanical strengthening at high temperature can be of a level as high as for cobalt alloys. Furthermore, the ferritic structure of the matrix of these iron-based alloys is mechanically weak at high temperature, due to its low crystalline compactness. Concerning the nickel-based alloys, TiC, TaC and NbC meet the concurrence of chromium carbides, with as result a co-existence of MC and Cr_xC_y in the microstructure, and even a total absence of MC in some cases (i.e. for 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 Cr_2Nb 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.

The benefit of the script-like shape of MC carbides for the creep resistance at elevated temperature was demonstrated less [12, 26] or more [27] recently, by comparison between the deformation rates of alloys with a rather high fraction of MC carbides and alloys of the same compositions and tested in the same conditions with less such MC carbides or with chromium carbides instead.

5. 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 that the previous observations – limited to cobalt-chromium systems – allowed to think [28]. Chromium carbides may be unexpectedly thermodynamically favored in some cases and when MC successfully forms, this is not necessarily with the morphology which is the most favorable to high mechanical resistance at elevated temperature (TaC in Fe-30Cr alloys, [29]). 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 [30] which would obstruct their use rather than the failure of precipitation of MC carbides during solidification.

This overview of all these as-cast microstructures which has allowed a preliminary exploration of the as-cast microstructures for a wide range of {M'(Cr) × MC-former element}- systems, must be now followed by thorough investigations for understanding the intrinsic differences of behavior between these metallurgical systems which lead to so evident microstructure differences between the different families for a given type of MC-former element and inside a given family for different MC-former elements. First results are currently available but numerous other phenomena remain to be explained.

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