# New polycrystalline MC-reinforced nickel-based superalloys for use at elevated temperatures (T > 1100°C)

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### Abstract

In some high temperature applications, there is a constant need of refractory alloys able to resist oxidation by hot gases, hot corrosion by various melts and creep deformation. The best superalloys are currently the  $\gamma/\gamma'$  nickel-based single crystals but they cannot be exposed to 1200°C and more without losing their mechanical resistance. New principles of conventionally cast polycrystalline nickel alloys, combining good resistance against both hot gas oxidation and melts corrosion are explored in this work. Among them, the most promising system involves a reinforcement by HfC carbides. The studied alloy has kept its chromia-forming behaviour which allows good resistance against both oxidation resistance and corrosion by melts. Interesting for a nickel-based alloy containing no  $\gamma'$  precipitates, its creep resistance at 1200°C still remains to be improved to allow using it at so high temperature. Copyright © 2017 VBRI Press.

Keywords: Nickel alloys, MC carbides, high temperature, oxidation, creep.

#### Introduction

Many applications at high temperature require the use of refractory materials which can be ceramics of metallic alloys. When tensile stresses may be encountered here or there, at a moment or at another one, metallic alloys must be preferred. This is the case of turbine blades in aeroengines or power generation plants as well as glass forming industrial tools, examples chosen among numerous ones. If some of the refractory metallic alloys for such uses are known since many decades ago and are still employed today [1, 2], metallurgical research and development works are currently intensive to satisfy the more and more exigent requirements in terms of surface and bulk stability at service temperatures which do not stop increasing: more and more severe environments (complex mixtures of oxidizing gases, corrosive molten sulfates mixtures or molten CMAS, aggressive molten glasses... depending on local temperatures) and combinations of simultaneous intensive applied mechanical stress (high amplitude tensile stresses, shear, creep, fatigue...). One of the most important family of refractory alloys developed in the last decades and remaining among the best efficient ones for particularly exigent applications is the one of the  $\gamma/\gamma'$  nickel-based single crystals [3]. This now rather old principle of alloy's strengthening by intermetallic Ni<sub>3</sub>Al-type coherent precipitates initially successfully applied to nickel-based superalloys [4] is currently explored in cobalt-based superalloys [5, 6]. In parallel other axes are also investigated such as rhenium-containing cobalt-based alloys [7, 8] or refractory high entropy alloys [9].

Besides these really new metallurgical principles it recently appears that older alloy types - polycrystalline equi-axed carbides-strengthened superalloys – having many times proven their interest may be rethought by replacing the usual chromium or chromium & tungsten carbides by MC carbides, for example in chromium-rich cobalt-based alloys [10]. In such Cr-rich Co-based alloys these MC carbides fortunately crystallize at the end of solidification as eutectic script-like carbides mixed with the periphery of the matrix dendrites. Furthermore, during new exposures at high temperatures this morphology, favorable to high mechanical properties at elevated temperatures, stays more (TaC, HfC, ZrC) or less (NbC) unaltered [10]. Unfortunately such cobalt-based alloys are only poorly resistant against high temperature oxidation despite the 30wt. % Cr that they contain [11]. This being due to the fact that chromium, element more polyvalent than aluminum since it normally allows resisting not only oxidation by gases but also corrosion by melts [12], diffuses less easily in a cobalt matrix than in a nickel matrix [13].

1200°C is a temperature at which the  $\gamma$ ' precipitates will be shortly totally dissolved because this temperature is still higher than the  $\gamma$ ' solvus one for both nickel-based and cobalt-based alloys. Thus, the  $\gamma/\gamma$ ' nickel-based single crystals become themselves mechanically weak. In contrast some of the MC carbides are still present even after a long time spent at so high temperature [10]. On another hand the hot oxidation behaviour of the cobaltbased matrixes are intrinsically rather bad, in contrast with the nickel bases. Iron matrix rich in chromium rather well behave in oxidation at high temperature but the back centered cubic crystallographic network that the required amounts in chromium (bcc-favoring element) brings to iron at high temperature while it is austenitic when alone (face centered cubic), makes it particularly mechanically weak.

Thus, associating a mechanically strong enough and well oxidation resistant matrix of nickel (austenitic despite the presence of several tens of wt.% Cr, and easy diffusion for Cr), with morphologically very stable MC carbides offering a script-like shape imbricated with dendrites probably favorable to high mechanical resistance at elevated temperature, may led to innovative superalloys responding the double mechanical and chemical demand for applications at high temperature. The purpose of this work is precisely starting to explore such new systems.

## Experimental

#### Choice of the MC-forming elements to study

Many elements belonging to the transition metals of the Mendeleiev table allow forming MC carbides: hafnium, niobium (or columbium), tantalum, titanium, vanadium, tungsten, zirconium... list to which one can also add chromium (able to form  $Cr_7C_3$ ,  $Cr_{23}C_6$  or  $Cr_3C_2$ , and CrCtoo) and rather exotic elements when one talks about superalloys: thorium, uranium... These elements do form MC carbides which are particularly stable as suggested by Ellingham diagrams. This is expected that they form preferentially to carbides of the base element and to chromium carbides. The room temperature hardness and melting points of these MC carbides are very high but the volume mass of which may vary significantly element by element. For the latter point of view the TiC carbides appear as being particularly interesting for the total density of the alloys while this is the contrary for the TaC carbides. The volume fraction of these carbides must remain low anyway, to allow the alloys keeping high impact toughness and to prevent too intense problems of mechanic interactions at the microstructure scale between the high thermal expansion matrix ( $\alpha$  of about 15 ×10<sup>-6</sup> K<sup>-1</sup>) and low thermal expansion MC carbides.

Hf is sometimes added to superalloys or protective coating alloys to enhance oxidation resistance [12, 13]. It is key element in the DS200-Hf directionally solidified superalloy [14]. It is recognized that its addition may influence the microstructure [15] and the properties [16] of superalloys. Niobium, which is considered for superalloys from several decades [17] can be found in substitution in to Al in the gamma prime particles

reinforcing the nickel-based single crystals [3] but it can be taken as the base element of recent superalloys [18]. Tantalum is used since a long time, for example in the MarM-509 cobalt-based superalloy [1, 2] and it was more recently used in rather great quantities to obtain high amounts in script-like TaC carbides in model cobalt-based [19, 20] or iron-based cast alloys [21, 22]. Titanium, also a  $\gamma$ '-former element as Al and Nb, may be a base element as in the famous TA6V alloy [23] or involved in different types of aluminides for high temperatures [24]. Vanadium and tungsten, due to their high oxidability and to the fact that their oxides  $(V_2O_5, WO_3)$  are volatile at not so high temperature, will not be considered here. Zirconium, which can be present in the chemical compositions of superalloys base on nickel [25] or on cobalt [26] is also the main element of the famous Zircalloy-4 [27].

#### Chemical compositions of the studied alloys

The selected MC-former elements were thus hafnium, tantalum, titanium and zirconium. Because of the too low morphological stability at elevated temperature in a cobalt-chromium alloy and its deleterious effect on the high temperature oxidation behavior of the same alloy, niobium was not kept in this work. A high chromium content, ranging between 25 to 30 wt.%Cr, high enough in nickel-based alloys to ensure a chromia-forming behavior, was chosen for the alloys. The carbon content was limited to 0.2 to 0.25 wt.%C to avoid having interdendritic carbide networks too interconnected. Finally, the M eight contents in Hf, Ta, Ti or Zr were rated to have the same atomic content as carbon. For comparison purpose, two ternary alloys, a Ni25Cr0.25C and a Co-25Cr-0.25C, reputed for their good oxidation behavior and creep resistance, respectively, were added to the study. The given names and chemical compositions of all these alloys are given thereafter:

"NiCrC=Ta": Ni(bal.)-30Cr-0.20C-3Ta "NiCrC=Ti": Ni(bal.)-25Cr-0.25C-1Ti "NiCrC=Hf": Ni(bal.)-25Cr-0.25C-3.7Hf "NiCrC=Ta": Ni(bal.)-25Cr-0.25C-1.9Ta "Ni25Cr0.25C": Ni(bal.)-25Cr-0.25C "Co25Cr0.25C": Co(bal.)-25Cr-0.25C all contents being in weight percent.

#### Elaboration

All alloys were elaborated by classical foundry, using a high frequency induction furnace (CELES, France). Charges were prepared from parts of pure elements (Ni, Cr, Hf, Ta, Ti and Zr from Alfa Aesar, and C as graphite, purity > 99.9 wt.% for all elements). For each elaboration the corresponding parts of the different elements were placed together in the copper crucible (cooled by internal water circulation), a silica tube was placed around, and three {pumping until primary vacuum, introduction of pure Ar}-cycles were applied. To finish, a pressure of 30mbars of pure argon was generated before heating. The latter operation took about 3 minutes until obtaining the whole alloy in the liquid state.

Homogenization in the liquid state was carried out isothermally, thereafter followed by cooling by decreasing the injected power until zero. Solidification took about thirty seconds and cooling to room temperature took about 30 minutes.

## Preparation of the samples for the different tests

The obtained ingots were cut in several parts using a metallographic cutter (Abrasimet of Buehler). This allowed obtaining, on the one hand, parts for the ascast microstructure observations and parts to perform high temperature exposures, and one the other hand, parts to be more accurately machined for the oxidation tests and the creep tests. The samples for the oxidation tests and for the creep tests were prepared as about 8 mm  $\times$  8 mm  $\times$  3 mm parallelepipeds and 15 mm  $\times$  2 mm  $\times$  1 mm parallelepipeds respectively. The first ones were ground with 1200-grit SiC papers with smoothing of their edges and corners while the second ones were only ground on their six faces (SiC 1200-grit papers), then polished (textile enriched with 1µm hard particles) until mirror-like state, with reaching high dimensional accuracy all along the samples (less than ±0.01 mm of thickness and of width variation from one extremity to the other one).

#### Description of the applied tests

First the samples prepared for the high temperature oxidation were placed in a tubular furnace, then heated up to 1200°C, maintained at 1200°C during 46 hours then cooled. The objective was to have a look to how had evolved the microstructures during this high temperature stage.

Each sample destined to the oxidation test was placed in the hottest zone of a thermobalance (TGA 92.16-18 of SETARAM, France), hung to a precision microbalance in a 1.5L/h flow of synthetic air (80%N<sub>2</sub>-20%O<sub>2</sub>), then heated at a constant rate of +20K/min until reaching 1200°C. After 46 hours of isothermal oxidation at 1200°C they were cooled at a constant rate of -5K/min, slow enough to allow minimizing the risk of oxide scale spallation. The weight versus time files were thus plotted to visualize the type and rate of mass gain kinetic. After having been photographed, the oxidized samples were coated by cathodic pulverization of gold, by a {2 hours, 1.6A/dm<sup>2</sup>}-electrolytic nickel deposition in a Watt's bath heated at 50°C (Ni thickness high enough to protect the scales during handling and cutting), then cut in to parts to prepare cross-sectional metallographic samples

Each sample devoted to the creep tests were placed in a thermodilatometer (TMA 92.16-18 of SETARAM, France) equipped with a special apparatus allowing three-points flexural creep. Placed on two bottom supports separated from one another by 12mm, a central top support applied a load calculated to induce a tensile stress of 20 MPa in the middle of the bottom face of the sample, taking into account the exact values of sample thickness and width. Heating was done at a constant rate of +20K/min, up to 1200°C. This temperature was maintained constant until the middle of the bottom part.of

the deforming sample entered in contact with the apparatus basis (after a deformation of about 1.4 mm). Cooling was then achieved at -20K/min. The creep curves were plotted as deformation (central point displacement) versus time.

#### Metallographic preparation

For each alloy, the as-cast part, the two halves of the aged part, and the two halves of the oxidized sample were embedded in a cold resin mixture (ESCIL, France), ground with SiC papers from 240-grit up to 1200-grit. After ultrasonic cleaning they were polished until obtaining mirror-like state with textile enriched with 1 $\mu$ m hard particles, and observed using a Scanning Electron Microscope (SEM) under a 20kV acceleration voltage in the Back Scattered Electrons mode (BSE). Energy Dispersion Spectrometry (EDS) global analyses and spot analyses were performed to control the alloys' chemical compositions and the phases' compositions.



**Fig. 1.** SEM/BSE micrographs illustrating the microstructures of: (a) the "NiCrC=Ta" alloy as-cast (top) and aged at  $1200^{\circ}$ C (bottom), and (b) the "NiCrC=Ta" alloy as-cast (top) and aged at  $1200^{\circ}$ C (bottom).

#### **Results and discussion**

The as-cast and aged microstructures

All the solidified NiCrC=M alloys are composed of a dendritic matrix and of interdendritic carbides. The matrix is, in all cases, a face centered cubic solid solution of nickel containing the greatest part of the chromium present in the alloy, and a more (case of Ta or Ti), or less (Hf, Zr) high quantity of the M element. As expected the interdendritic carbides are almost exclusively of the HfC or ZrC type in the NiCrC=Hf or NiCrC=Zr alloys, respectively. In contrast, they are only partly of the TaC type in the as-cast NiCrC=Ta alloy in which chromium carbides are also present, and almost none of them are of the TiC type in the NiCrC=Ti one which contains essentially chromium carbides.

After about 50 hours of isothermal exposure at 1200°C, the initially existing TaC carbides had totally disappeared in the NiCrC=Ta alloy (**Fig. 1(a**)), chromium carbides being now the single type of present carbides, while the rare TiC earlier observed in the as-cast microstructures are now inexistent in the NiCrC=Ti alloy (**Fig. 1(b**)).



**Fig. 2.** SEM/BSE micrographs illustrating the microstructures of: (a) the "NiCrC=Hf" alloy as-cast (top) and aged at  $1200^{\circ}$ C (bottom), and (b) the "NiCrC=Zr" alloy as-cast (top) and aged at  $1200^{\circ}$ C (bottom).

The HfC carbides did not suffer from the high temperature exposure, neither in term of morphology nor in term of surface fraction, even if some rare chromium carbides appeared besides them (Fig. 2(a)). No such chromium carbides precipitated in the NiCrC=Zr alloy during the same high temperature exposure but the morphology of the initial ZrC carbides significantly evolved: they coalesced to become rounder (Fig. 2(b)).

## Selection of alloys for further high temperature properties characterization

The NiCrC=Ta and NiCrC=Ti alloys, which did not contain exclusively MC carbides in their as-cast conditions and which demonstrated verv low thermodynamic stability of their microstructures at high temperature with the disappearance of the MC carbides, were not selected for further investigations. Indeed, these alloys are not able to contain MC carbides for long times at high temperature and the chromium carbides which may strengthen them are well known to be not stable enough to replace MC carbides in this role since they rapidly decrease in volume fraction and they lose their initial elongated shape to become round and coarse as soon as temperature is higher than 1100°C (and even 1000°C for long times). In contrast, in the volume fraction field, the NiCrC = Hf and NiCrC = Zr alloys appeared above to be much more suitable for uses at elevated temperature. However the zirconium-containing alloy will be removed from the selection because of the very fast coarsening which affected their initial morphology after only about fifty hours at 1200°C. The single remaining alloy available for the oxidation and creep tests is consequently the NiCrC = Hf alloy.



**Fig. 3.** Surface states of a reference Ni-25Cr-0.25C alloy oxidized in air at 1200°C for 46h and cooled at  $-5^{\circ}$ C min<sup>-1</sup> (a) and of the "NiCrC=Hf" alloy oxidized and cooled in the same conditions (b).

Behavior of the single selected alloy in high temperature oxidation

A part of the NiCrC = Hf alloy was used to prepare a thermogravimetry sample which was thereafter exposed in a flow of synthetic air at  $1200^{\circ}$ C during 46 hours inside the thermo-balance. After this high temperature

isothermal stage, and the cooling at -5K min<sup>-1</sup> down to room temperature, the tested sample was exited from the apparatus and first visually analysed. By comparison with a model NiCrC ternary alloy with the same Cr and C contents, synthesized following the same elaboration/sample preparation procedures and oxidized in accordance with the same test protocol (used thermbalance, gas, thermal cycle), it clearly appears that the oxides formed all around the oxidized NiCrC = Hf sample remained in its surface, in contrast with what occurred during the cooling for the oxidized Ni25Cr0.25C alloy (**Fig. 3**).

For this later alloy, the oxide scales did not well resist the thermo-mechanical interfacial stresses induced by the thermal expansion coefficient mismatch between oxide scale and metallic substrates, this resulting in spallation of the external oxide scales during cooling, with as consequence about half of surface having lost its oxide scale (these denuded metallic areas are the white zones on the sample surface). The NiCrC = Hf behaved much better in this first point of view (no denuded parts of alloy).



**Fig. 4.** Mass gain curves of the reference Ni-25Cr-0.25C alloy and of the "NiCrC=Hf" alloy during their oxidation in air at 1200°C for 46h.

The thermogravimetry curve drawn with the recorded mass gain variations file is plotted versus time in Fig. 4, together with the one of the ternary Ni25Cr0.25C reference alloy. As for this later alloy, well known for its very good behavior in high temperature oxidation, the oxidation regime of the NiCrC = Hf alloy is of the parabolic type and then oxidation obeys the Wagner's law. In addition the mass gain curve is unaffected by any mass gain jumps, showing that the isothermal scale adherence was already good. The parabolic kinetic suggests that the external oxide scale was always continuous, as visually observed above after test, and protected the alloy from fast linear oxidation. Initially fast, the oxidation was thus slower and slower. The behavior in oxidation of the NiCrC = Hf alloy was even better than the Ni25Cr0.25C alloy's one since the mass gain rate was lower at all times. At the end of the 46 hours

isothermal stage the mass gain was only about  $2.1 \text{ mg cm}^{-2}$  against 2.7 mg cm<sup>-2</sup> for the Ni25Cr0.25C alloy.

Two micrographs taken at two different magnifications are presented in Fig. 5. The ×250 one (a) allows an enlarged view of the oxidized surface and a general examination of the subsurface microstructure: this one is seemingly not affected by the {1200°C, 46h}-stage in air. The  $\times 1000$  one (b), magnification at which EDS spot analyses were also carried out, evidences the real subsurface state close to the interface: the hafnium carbides located very close to the oxide/alloy interface were oxidized in situ, converted in HfO<sub>2</sub> internal oxides, appearing white and thus looking like HfC carbides. However, a little deeper and of course also deeper in the bulk, the white particles are still HfC. They are morphologically not affected by the high temperature exposure. EDS spot analyses were also performed on the grey oxides: the external layer is, as for the ternary reference alloy, mainly chromia (Cr2O3) although some areas of spinel oxide (NiCr2O4) were also detected.



Fig. 5. Surface and subsurface states of the "NiCrC = Hf" alloy after its oxidation in air at 1200°C for 46h, observed at two magnifications:  $\times 250$  (a) and  $\times 1000$  (b).

## Behaviour of the single selected alloy in high temperature creep

The NiCrC=Hf alloy was also subjected to a 3 points flexural creep test, at 1200°C too, with a load rated to induce a tensile stress equal to 20 MPa in the middle of the bottom side of the parallelepiped sample. A micrograph of this sample before test and another one of the same but after tests are shown in Fig. 6(a), together with a micrograph of a reference Co25Cr0.25C sample having been subjected to the same test (same temperature and same induced maximal tensile stress, but much longer time). One can see that the NiCrC=Hf alloy is much more deformed than the ternary cobalt alloy despite the shorter duration of test of the nickel alloy. The NiCrC=Hf alloy has obviously deformed faster than the cobalt alloy, as confirmed by the deformation curves drawn from the recorded displacement of the middle upper support (Fig. 6(b)). This is due first to a longer and faster primary stage of creep for the NiCrC=Hf alloy than for the cobalt alloy, and second to a secondary creep rate itself faster than the cobalt alloy's one. The bottom part of the nickelbased sample went in contact with the base of the alumina support (displacement of 1.4 mm) after nearly 25 hours. In the same time the deformation of the cobalt alloy was less than 0.3 mm.

![](_page_5_Figure_5.jpeg)

Fig. 6. Results of flexural creep tests:

(a) the deformed and oxidized states of a reference Co-25Cr-0.25C alloy (after 100 hours, left) and of the "NiCrC=Hf" alloy (25 hours before contact, right) after creep test at 1200°C under a load applied on the top middle to induce a 20 MPa tensile stress.

(b) the first parts of the deformation curves of the reference Co-25Cr-0.25C alloy (left) and of the "NiCrC=Hf" alloy (right) recorded during creep tests at 1200°C under a load applied on the top middle to induce a 20 MPa tensile stress.

#### Discussion

The first comment that can be done about the present experimental results is the confirmation that the thermodynamic stability of isolated carbide particles can be first estimated by its formation free enthalpy for the comparison with other types of carbides, but that it is also strongly dependent on the environment (the matrix) with which carbides constitute the thermodynamic system. Thus, although very stable at high temperature when in presence of chromium, TaC and TiC are not in equilibrium with a nickel-chromium matrix, the most stable microstructure state being matrix (containing Ta or Ti) with chromium carbides. This is totally different from what was previously observed in cobalt-based and ironbased chromium rich alloys. In contrast the HfC and ZrC carbide phases are indisputably more stable than chromium carbides in such nickel-chromium base. But, to be efficient against creep deformation, the MC carbides must keep a long time at high temperature their script-like morphology inherited from the crystallization mechanisms. This morphology, which is the strong point of MC carbides since it allows them insuring interdendrites cohesion and delaying the third stage of creep, is rapidly lost by the ZrC carbides in this nickelchromium base. Consequently, the HfC carbides remain the single available MC-reinforcement system among the four studied ones.

When creep test was run at the particularly high temperature of 1200°C for a significant tensile stress of 20 MPa, one saw that the deformation rate of the NiCrC=Hf alloy was rather fast, notably by comparison with a simple ternary Co25Cr0.25C cobalt-based alloy strengthened by only a few chromium carbides. By reminding that it is well known that a simple nickelchromium alloy is less strong than a cobalt-chromium one at high temperature as well as at low temperature, this is not surprising. Indeed, a cobalt base is intrinsically harder than a nickel one, and the secondary creep of the later is necessarily faster than the secondary creep of the former. The benefit of the interdendritic HfC carbide network is expected essentially for the transition secondary stage  $\rightarrow$ tertiary stage, and this was not possible to observe this effect because of the contact between sample and apparatus base occurred before the end of the secondary This highlights that the resistance of the creep. NiCrC=Hf alloy must be improved to allow observing the stage transition between secondary and tertiary and then the global kinetic of this tertiary creep. For that, enrichments in heavy atoms of the matrix of the Ni-Cr matrix or precipitation treatments can be later studied to reinforce the matrix by solid solution strengthening and/or secondary carbides. Such time-consuming work merits to be carried out since it may lead to very interesting superalloys, easy to elaborate (even into geometrically complex pieces: conventional casting, equiaxed alloys) and intrinsically resistant against both high temperature oxidation by gases and corrosion by melts (nickel base, high content in chromium). This later point is not easily achievable with cobalt alloys even enriched with chromium. Additionally, one can remind, besides the very good oxidation behavior of this Ni25Cr0.25C3.7Hf base, its remarkable resistance against oxide spallation at cooling, and then probably also against thermal cycling. This well-known effect of hafnium for low contents of this element is found again for this particularly high content of 3.7 wt.%.

#### Conclusion

This systematic work carried out on a nickel-chromium base with addition, step by step, of MC carbides of successive types, allowed discard different possible {nickel-chromium-matrix, MC} systems test after test (as-cast microstructure, microstructure behavior at high temperature, high temperature oxidation run and high temperature creep). This allowed converging to a simple alloy Ni-25Cr-0.25C-3.7Hf (all contents in wt.%) which is constituted of an interdendritic network of eutectic script-like HfC carbides remarkably stable at high temperature - potentially efficiently strengthening - and of a matrix bringing an intrinsically high resistance against chemical aggressiveness of the high temperature gaseous or molten environments. Even if further work remains to be achieve to go on progressing in the general high temperature properties (by complexifying the chemical composition with the introduction of heavy elements, and the elaboration route by adding post-casting heat-treatments), it seems that the simple association of a nickel-chromium base and a carbide network exclusively composed of HfC is a rather smart principle. Taking into consideration that  $\gamma/\gamma$ ' single crystalline nickel-based superalloys lose their  $\gamma$ ' precipitates, then their mechanical superiority at temperatures higher than 1100°C, such HfC-reinforced nickel-based superalloys may represent a credible alternative after their optimization.

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