Mechanical and Chemical Properties at High Temperature of {M-25Cr}-based Alloys Containing Hafnium Carbides (M=Co, Ni or Fe): Creep Behavior and Oxidation at 1200°C

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Abstract: This study concerns three alloys based on cobalt, nickel or iron, all containing chromium (25 wt.%), carbon and hafnium. The contents in the two last elements were chosen high enough to promote the formation of HfC carbides. All alloys were elaborated by casting and their microstructures preliminarily characterized. They were selected to be tested in three-points flexural creep at 1200°C under 20 MPa in inert atmosphere. All alloys contain hafnium carbides, together with chromium carbides in some cases. The HfC carbides are generally of two types: script-like eutectic and blocky pre-eutectic. The creep deformation is fast for the nickel-based and iron-based alloys, especially for the later one. In contrast the HfC-containing cobalt-based alloy behaves much better. It displays a creep resistance at 1200°C significantly higher than another cobalt-based alloy strengthened by chromium carbides added to the study for comparison. All alloys were also briefly tested in oxidation by air at 1200°C. The creep behaviors of the cobalt-based and iron-based alloys are not good and significantly worse than the nickel-based alloy's one. The oxidation resistance of the HfC-strengthened cobalt-based alloy must be improved to take benefit of its superior creep strength.

Keywords: Cast alloys, Cobalt, Nickel, Iron, HfC carbides, High temperature, Bending tests, Creep resistance, Oxidation.

1. INTRODUCTION

Many metallic pieces working in the hottest zones of the aero-engines, the energy production plants or other industrial processes (e.g. turbine blades, glass-fiberizing tools…) must be made of refractory alloys with high mechanical properties at elevated temperature. Superalloys generally meet these requirements [1], notably the γ/γ' single crystal directionally solidified alloys [2]. Unfortunately high temperatures generally induce problems of fast dry oxidation (by oxidant gases) and hot corrosion (by aggressive molten substances). In the later case, the presence of high chromium contents in alloys is compulsory [3]. In such cases the alloys must be structurally strengthened following other ways than precipitated gamma prime particles: solid solution strengthening, carbides…

In the case of the superalloys produced by classical foundry (inert atmosphere but equi-axed solidification) carbides may strengthen both grain boundaries (interdendritic carbide-matrix eutectic) and grains (dispersed fine secondary carbides). To be efficient at high temperature on long times the obtained carbides must be very stable. In this field tantalum carbides (TaC) are interesting because of their high thermodynamic stability at high temperature better than the chromium carbides one. But they progressively become fragmented and their volume fractions tend to decrease, during high temperature service. This was for example observed in cobalt-based alloys [4] and iron-based ones [5] (rather slow fragmentation) while the TaC phase rapidly disappeared in nickel-based alloys [6] in which they are in contrast less stable that the chromium carbides.

Other MC-type carbides – HfC carbides – showed a better stability, first in chromium-rich cobalt-based alloys [7], but also in nickel-based and iron-based ones [8]. Such carbides were obviously rarely considered for the strengthening of refractory metallic alloys, since few publications mentioned or studied such use of HfC carbides. One can cite the cases of molybdenum [9], cobalt [10] or nickel [11-13] alloys. Cobalt-based, nickel-based and iron-based alloys rich in chromium and containing carbon and hafnium in quantities high enough to promote the development of HfC carbides at solidification were previously elaborated and exposed at 1200°C during about 50 hours [8]. Their metallographic study before and after high temperature exposure revealed that the HfC carbides remained almost unchanged, which let think that the mechanical strengthening potential of these carbides did not evolve. The purpose of the present work is now to characterize the real mechanical behavior of these alloys at high temperature, by performing at 1200°C bending tests under constant load.

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2. MATERIALS AND METHODS

2.1. Alloys Under Study

The alloys considered in this work are three alloys elaborated by foundry, from pure elements (Co, Ni, Fe, Hf from Alfa Aesar, purity > 99.9 wt.%). Their fusion and solidification both took place in the water-cooled copper crucible of a High Frequency Induction furnace (CELES) under an inert atmosphere of 300 mbars of pure Ar. The obtained compact ingots (mass: about 40g) were cut using first a Buelher Delta Abrasimet cutter and second a Buelher IsoMet 5000 precision saw. Initially two types of samples were generated: compact ones for the metallographic characterization of the as-cast microstructures of the alloys, and elongated parallelepipeds for the bending tests. The first ones were cut and embedded in cold resin (ESCIL: CY230 resin and HY956 hardener). They were ground with SiC papers from 250 to 1200-grit, ultrasonically washed, then polished with textile enriched with 1µm hard particles. The second ones, with as dimensions 1mm (thickness) × 2mm (width) × 15mm (length), were carefully prepared by accurate cutting. They were polished with papers up to 1200-grit with final strips in the length direction. These parallelepipeds, with constant thickness and width (tolerance: ±0.01mm, measurements carried out using an electronic caliper), underwent additionally visual inspection followed by thorough microscopy examination (optical, and sometimes electronic) to detect eventual defects able to weaken the samples. Additional samples were also cut to perform high temperature oxidation tests to complete the characterization: parallelepipeds of about 8mm × 8mm × 3mm polished all around with 1200-grit SiC papers with smoothing of edges and corners.

2.2. Microstructure Examinations

The embedded and polished samples were observed using a Scanning Electron Microscope (SEM): a JEOL JSM6010LA one. Observations were done under an accelerating voltage of 20kV, mainly in Back Scattered Electrons mode (BSE) and at different magnifications between ×125 and ×1000). The real chemical composition of the alloys was measured using the Energy Dispersive Spectrometry (EDS) device equipping the SEM, and the different phases were identified by EDS spot analyses.

2.3. Hardness Measurements and Bending Tests at High Temperature

First the hardness of the three alloys at room temperature was measured using a Testwell apparatus according to the Vickers method and by applying a load of 30kg. For each alloy three indentations were performed for calculating an average value and a standard deviation one.

The bending tests were done according to the symmetrical three points method. They were carried out by using a high temperature dilatometer (SETARAM, TMA92-16.18) modified to allow 3-points flexural testing (alumina equipment supplied by SETARAM), in an inert atmosphere (pure Ar). The space between the two bottom supports was 12mm and the height of these supports was about 2mm (thus maximal possible deformation). The load applied to the sample by the upper support was accurately calculated for each sample by taking into account the exact values of their thickness and width. As example, the applied load was 200.16g for the CoHFC sample (chemical composition in Table **1**) the section of which was thickness 0.93mm × width 2.05mm. The load was progressively applied at room temperature and the whole heating (done at 20°C min^{-1}) was realized while the load constantly pressed on the sample. The displacement of the upper support was recorded every 36 seconds during the whole experiment: heating, isothermal dwell at 1200°C during 100 hours and cooling (rate: -20°C min^{-1}).

Table 1: Chemical Compositions of the Alloys as Measured by EDS

Alloy designation	Base element	Cr	Hf
CoHFC	cobalt	25	10
NiHFC	nickel	25	7
FeHFC	iron	27	5

2.4. Oxidation Tests

To complete this experimental work some simple oxidation tests were performed to have a look to the thermochemical behavior of the studied alloys when exposed to another solicitation often occurring in service: oxidation by hot gases. Per alloy a parallelepiped sample with smoothed edges and corners was exposed to synthetic dry air 80%N_2-20%O_2 in a furnace during about 50 hours at 1200°C after a heating at 20°C min^{-1} and before a cooling at -5°C min^{-1}). The oxidized samples were thereafter embedded by a thin gold coating then by a thicker nickel coating (electrolytic). This was done in order to mechanically protect the oxide scales. They were cut and, as the previous samples for metallography observations, embedded with cold resin and polished until obtaining a mirror-like state. They were examined using the SEM in BSE mode to observe the oxide scales which were identified by EDS analysis.

3. RESULTS

3.1. Chemical Compositions and Microstructures of the as-Cast Alloys

The chemical compositions of the three alloys, assessed by EDS measurements, are displayed in Table **1**. The three alloys contain around 26 wt.% of chromium (EDS) and 0.5 wt.% of carbon (targeted). It was not possible to measure the carbon content but one can reasonably think that it was well respected. Indeed, the elaboration protocole (atmosphere, heating rate, 3 minutes-dwell in the molten state, dwell temperature, cooling rate) followed for the synthesis of these alloys was rigorously the same as what it was previously done for many other alloys of the same category (except so high Hf contents): base elements, alloying elements and typical amount in carbon. For the ones among these previous alloys which were analyzed by spark spectroscopy the obtained carbon contents were very close to the targeted ones.

The CoHFC alloy (Figure **1**), containing 0.5 wt.% C and 10 wt.%Hf, present a microstructure composed of:

- a dendritic matrix of cobalt-chrome solid solution, free of hafnium
- an interdendritic network of hafnium carbides mixed with matrix
- supplementary hafnium carbides with a compact shape

The interdendritic HfC carbides are obviously of a eutectic nature and one can reasonably think that they precipitated at the end of solidification. The blocky HfC carbides, more precisely the rare ones which were trapped by solidification in the core of the ingot, probably precipitated at the beginning of solidification since the presence of many such carbides was noticed in the periphery of the ingot. These pre-eutectic carbides were obviously driven outwards by the electromagnetic stirring existing during the first part of solidification when the dendrites were not yet developed enough to obstruct this pro-eutectic carbides outward migration.

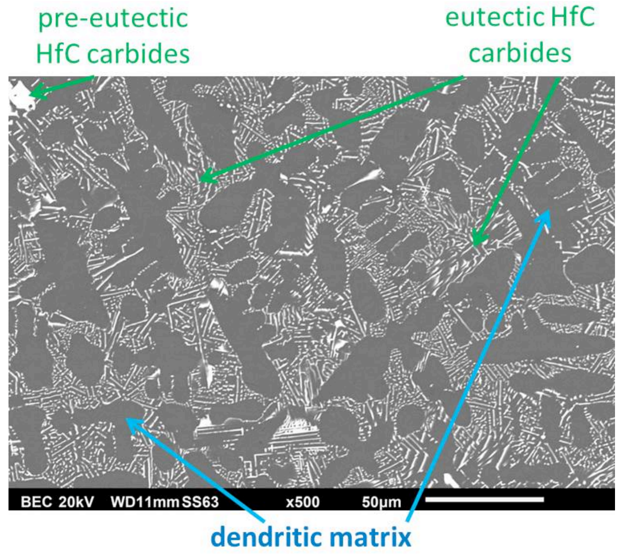

Figure 1: As-cast microstructure of the CoHFC alloy (SEM/BSE micrograph).

The NiHFC alloy, which was wished with less hafnium than for the previous cobalt alloy to try avoiding these pre-eutectic HfC carbides, also displays a dendritic matrix (of nickel-chromium solid solution) and only eutectic hafnium carbides (Figure **2**). These ones are present in the interdendritic spaces too, but in lower density than in the cobalt alloy. This is probably due to the lower hafnium content (7 wt.% Hf) which also allowed obtaining a slightly less interconnected carbides network than for the cobalt alloy. Some rare and small chromium carbides are also present here and there.

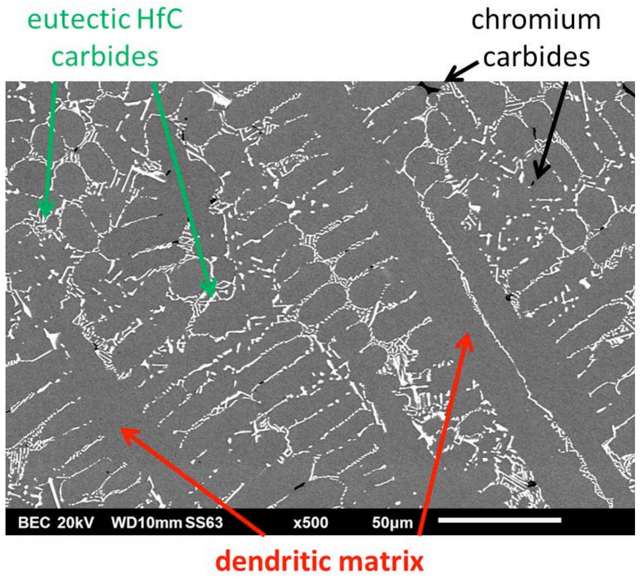

Figure 2: As-cast microstructure of the NiHFC alloy (SEM/BSE micrograph).

The FeHFC alloy (Figure **3**), also wished with a hafnium content lower than for the cobalt alloy (5 wt.% Hf) contains an interdendritic network of HfC carbides and much more chromium carbides than for the nickel alloy. The HfC carbides are obviously fragmented.

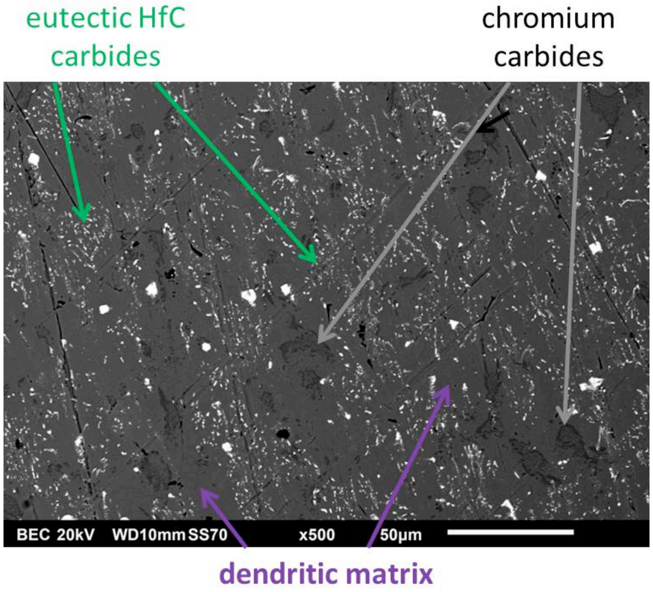

Figure 3: As-cast microstructure of the FeHFC alloy (SEM/BSE micrograph).

3.2. Mechanical Properties

3.2.1. Room Temperature Hardness

The results of indentation are presented in Table **2**. The cobalt alloy is the hardest one among the three alloys, with almost twice the value of these later ones. This can be due to its much denser carbide density but also to the intrinsically harder cobalt matrix. Despite its compact Face Centered Cubic (FCC) matrix and a carbide density rather high the hardness of the nickel alloy is significantly lower than the cobalt alloy's one. However the hardness of the nickel alloy is higher than the iron alloy one the matrix of which is intrinsically soft (Back Centered Cubic (BCC)) for a carbide volume fraction (HfC + chromium carbides) of the same order of magnitude as the nickel alloy.

Table 2: Room Temperature Hardness (Average and Standard Deviation Values from Three Vickers Tests Performed with a 30kg-Load)

Alloy designation	Average	Standard deviation
CoHFC	402	8
NiHFC	239	3
FeHFC	185	2

3.2.2. Creep Resistance at High Temperature

The three-points flexural creep tests were carried out for the three alloys at 1200°C for an equivalent traction stress of 20 MPa in the middle of the lowest face of the samples, by applying a load especially calculated for the section of each sample. The 1200°C-dwell duration was of 100 hours for the cobalt alloy and the nickel alloy while the test was shortened for the iron alloy. Indeed the later one deformed very rapidly, already during the latest part of heating, and the sample was in contact with the bottom of the alumina apparatus only few hours after the beginning of the 1200°C stage.

The whole alumina apparatus and a sample are shown by microphotographs in Figure **4**, before and after creep test. Photographs of the three samples before and after test are presented in Figure **5** in which one can see that the CoHFC sample is much less deformed than the NiHFC one for the same duration. The FeHfC alloy is as deformed as the NiHFC alloy but after only few hours after the 1200°C-dwell beginning.

The deformation curves are plotted in Figure **6**, only for the CoHFC alloy and for the NiHFC one (no plot of the too short FeHFC curve). One can see that the NiHfC alloy deformed rather rapidly and the middle of its bottom face met the alumina bottom after about 50 hours (half the whole test duration), with as result a final horizontal part in the deformation curve. In contrast the CoHFC alloy deformed much slowly and its curve clearly presents a primary stage and a secondary stage (linear) of creep. The secondary creep stage was not finished when the test was stopped at 100 hours.

For comparison another 3-points flexural test result obtained in the same geometry, thermal and stress conditions but for a cobalt-based alloy strengthened by chromium carbides is added. This one, tested for only 50 hours, well behaved and one can distinguish for it too a primary creep stage and a secondary creep stage. Obviously the presence of HfC carbides in the CoHFC brought a very efficient strengthening: secondary deformation rate six times lower for the CoHFC alloy than for the chromium carbides – strengthened alloy (which already deformed four times lower than the NiHfC alloy), as shown in Table **3**.

3.3. Oxidation

Despite that the creep tests were carried out in pure argon the traces of oxygen present led to a visible surface oxidation of the samples during the high temperature parts of the bending tests, as observed on the micrographs displayed in Figures **4** and **5**. Because

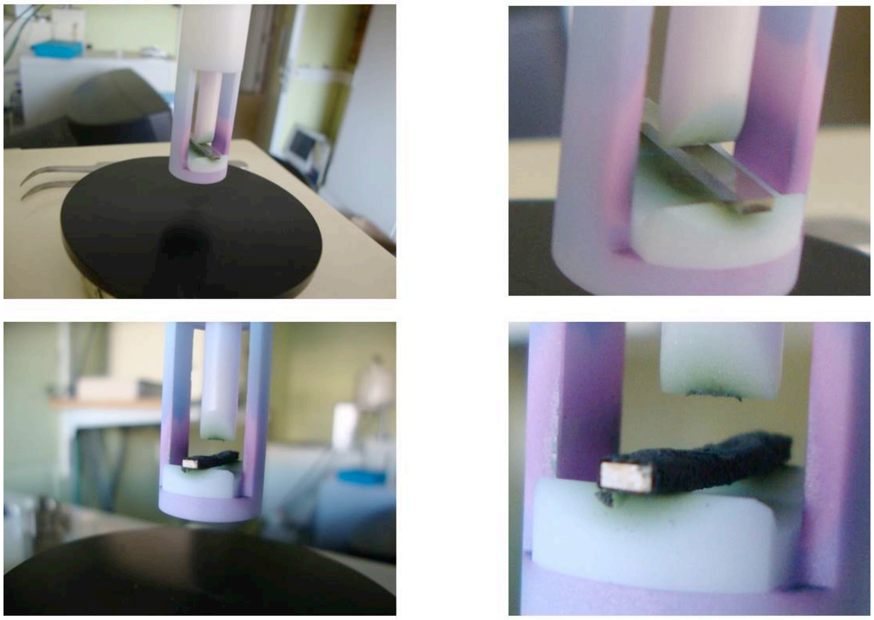

Figure 4: Photographs of the apparatus used for the bending creep tests; sample before test (top) and sample after test (bottom).

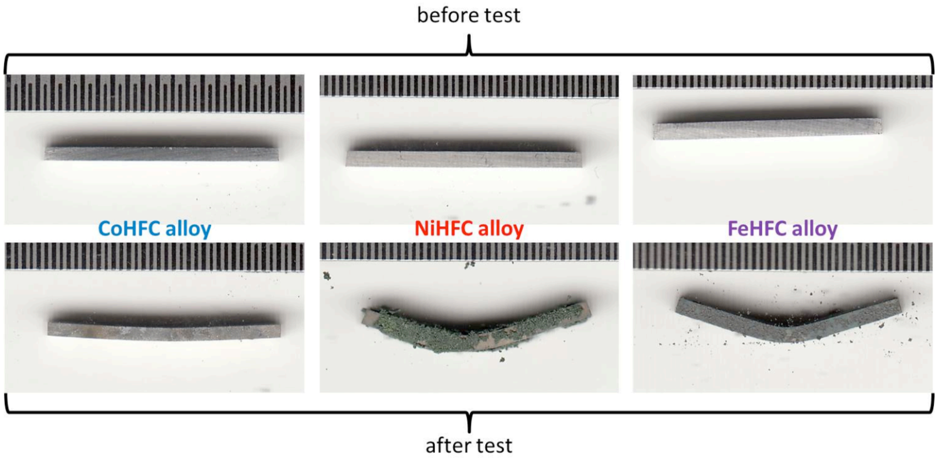

Figure 5: Photographs of the three samples before test (top) and sample after test (bottom).

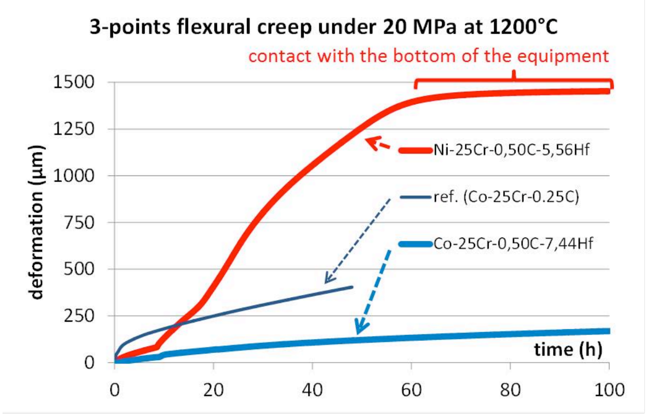

Figure 6: The obtained deformation curves (except the one of FeHFC which was too fast and stopped much sooner than 100h); comparison with the one previously obtained for a ternary cobalt-base alloy).

of the deformation progress (compression on the upper face and traction on the bottom face) and of the cooling (difference of thermal expansion or contraction between alloy and oxide) the oxide scales were mechanically solicited and they were lost at the aperture of the apparatus and during the handling of the tested samples.

To have a more thorough look to the behavior in high temperature oxidation additional thermal tests were carried out (exposure to air at 1200°C during about 50 hours). The SEM examination of the oxidized samples after metallographic preparation and the EDS spot analysis showed that:

Table 3: Values of some Parameters Characterizing the Deformation Kinetic of the Samples During the Creep Tests

Alloy designation	Start of the secondary creep stage (h)	Deformation rate during the secondary creep stage ($\times 10^{-3}$ µm s^{-1})
CoHFC	about 30	0.25
NiHFC	about 30	6.1
FeHFC	*deformation started during heating*	*sample already in contact with bottom only few hours after heating*
Ref. alloy	about 5	1.5

- the CoHfC alloy is covered by an external oxide scale generally composed of Cr_2O_3 (inner part, dark grey) and of spinel $CoCr_2O_4$ (outer part, pale grey), not particularly thick (Figure **7**), containing additionally small islands of HfO_2 oxides (white),

- the NiHfC alloy is covered by an external oxide mainly composed of Cr_2O_3 (dark grey) with also presence of small of HfO_2 oxides (white) immersed in this chromia scale (Figure **8**),

- the FeHfC alloy is covered by an external oxide scale much thicker than above for the two other alloys, and multi-constituted again (Figure **9**): inner layer of chromia, outer layer of complex oxide $(Fe,Cr)_2O_3$ with various Fe/Cr ratios, and also small HfO_2 oxides dispersed in the scale thickness, mainly in the outer layer of $(Fe,Cr)_2O_3$

This is in good agreement with what was observed on the oxidized surfaces of similar alloys based on cobalt [14], nickel [15] and iron [16] containing too high Hf quantities.

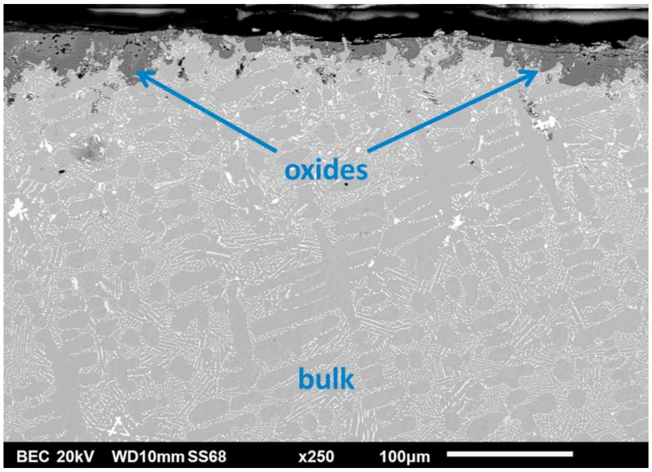

Figure 7: Sub-surface of the CoHFC alloy after 50h of oxidation in air at 1200°C.

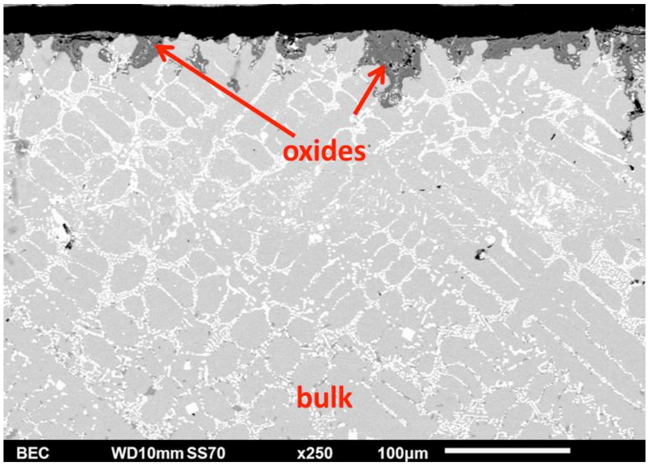

Figure 8: Sub-surface of the NiHFC alloy after 50h of oxidation in air at 1200°C.

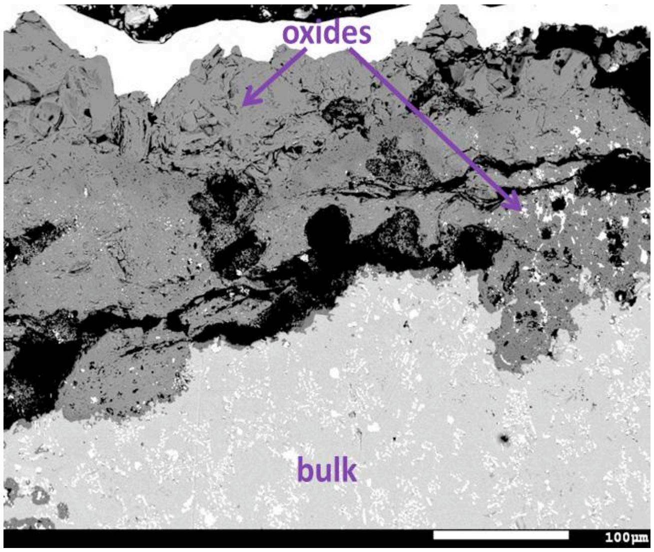

Figure 9: Sub-surface of the FeHFC alloy after 50h of oxidation in air at 1200°C.

4. DISCUSSION

Thus, when the hafnium content is very high the usual solidification scenario common to many alloys containing carbides, of the MC type notably, is a little modified. Indeed solidification starts with the crystallization of pre-eutectic carbides at high temperature, with as consequence the possible loss of a part of these carbides migrated on the ingot's periphery in case of high frequency induction melting. The phenomenon here encountered in the case of the too Hf-rich cobalt alloy was limited for the two other alloys by decreasing the Hf content. But the obtained eutectic HfC were consequently less dense. This led to hardness which were much lower for the nickel alloy and for the iron alloy, but the intrinsically lower hardness of the nickel and iron solid solutions were also responsible of these hardness differences observed among these alloys at room temperature.

As suggested by the room temperature hardness values the resistances of the three alloys were very different. The cobalt-chromium matrix, known to be more creep-resistant than nickel in absence of any hardening by intermetallic precipitation, associated with a dense interdendritic network of hard and very stable at high temperature HfC carbides, led to a very good behavior under stress at high temperature. Its remarkable creep resistance is considerably better than the nickel alloy and the iron alloy ones, is also significantly better than the one of the cobalt alloy strengthened by chromium carbides.

In contrast, if the intrinsically harder matrix of the cobalt alloy helped the CoHFC alloy in the high temperature mechanical field by comparison with the NiHFC and the FeHFC alloys, this is the nickel alloy which was the best in the high temperature oxidation field, helped by the intrinsically higher oxidation resistance of its nickel matrix. The cobalt alloy, the matrix of which is intrinsically worse than the nickel alloy one for the same chromium content, did not well behave during the 50 hours – oxidation test.

5. CONCLUSION

The cobalt alloy strengthened by a great quantity of HfC carbides presents a very interesting mechanical strength at high temperature, with a probable long sustainability. However, after only 50 hours of exposure to air at 1200°C, the surface of this cobalt alloy was deteriorated with the formation of no really protective oxides, which let think that catastrophic oxidation was imminent. It appears compulsory to increase its resistance against high temperature oxidation to allow benefiting of its high creep resistance. Increasing its chromium content may be a solution. This can be outlooks for next work.

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REFERENCES

[1] Sims CT, Hagel WC. The Superalloys, John Wiley & Sons: New York 1972.

[2] Donachie MJ, Donachie SJ. Superalloys: A Technical Guide, 2nd ed. ASM International: Materials Park 2002.

[3] Young D. High Temperature Oxidation and Corrosion of Metals. Elsevier Corrosion Series: Amsterdam 2008.

[4] Berthod P, Michon S, Aranda L, Mathieu S, Gachon JC. Experimental and Thermodynamic Study of the Microstructure Evolution in Cobalt-base Superalloys at High Temperature. Calphad 2003; 27: 289-294. http://dx.doi.org/10.1016/j.calphad.2003.12.003

[5] Berthod P, Hamini Y, Aranda L, Héricher L. Experimental and Thermodynamic Study of Tantalum-containing Iron-based Alloys Reinforced by Carbides: Part I-Case of (Fe, Cr)-based Ferritic Steels. Calphad 2007; 31: 351-360. http://dx.doi.org/10.1016/j.calphad.2007.01.007

[6] Berthod P, Aranda L, Vébert C, Michon S. Experimental and Thermodynamic Study of the Microstructural State at High Temperature of Nickel-base Alloys containing Tantalum. Calphad 2004; 28: 159-166. http://dx.doi.org/10.1016/j.calphad.2004.07.005

[7] Berthod P. High Temperature Properties of several Chromium-containing Co-based Alloys Reinforced by Different Types of MC Carbides (M=Ta, Nb, Hf and/or Zr). Journal of Alloys and Compounds 2009; 481: 746-754. http://dx.doi.org/10.1016/j.jallcom.2009.03.091

[8] Berthod P, Conrath E. Elaboration and Metallographic Study of {M-25Cr}-based Alloys Containing Hafnium Carbides (M=Co, Ni or Fe): Microstructures in the As-cast State and after Exposure at 1200°C. Advances in Alloys and Compounds 2014; 1(1): 3-14.

[9] Witzke WR. Composition Effects on Mechanical Properties of Hafnium Carbide-strengthened Molybdenum alloys. Metallurgical Transactions A: Physical Metallurgy and Materials Science 1976; 7A(3): 443-451. http://dx.doi.org/10.1007/BF02642842

[10] Nold E, Ondracek G. Investigations about the Structure of Interference Coatings on Gas-contrasted Hafnium Carbide-Cobalt Hard Metal. Praktische Metallographie 1986; 23(6): 268-276.

[11] Kim YG. A Directionally Solidified Nickel-base Eutectic Alloy Reinforced by a Mixed Hafnium-Zirconium Monocarbide. Journal of Materials Science 1978; 13(4): 759-765. http://dx.doi.org/10.1007/BF00570510

[12] Ribaudo C, Mazumder J. Oxidation Behavior of a Laser-clad Nickel-base Alloy Containing Hafnium. Materials Science & Engineering A: Structural Materials: Properties, Microstructure and Processing. 1989; A120-121: 531-538.

[13] Bouhanek K, Oquab D, Pieraggi B. High-Temperature Oxidation of Single-Crystal Nickel-based Superalloys. Materials Science Forum 1997; 251-254: 33-40. http://dx.doi.org/10.4028/www.scientific.net/MSF.251-254.33

[14] Berthod P, Conrath E. As-cast Microstructures and Behavior at High Temperature of Chromium-rich Cobalt-based Alloys Containing Hafnium Carbides. Materials Chemistry and Physics 2014; 143: 1139-1148. http://dx.doi.org/10.1016/j.matchemphys.2013.11.014

[15] Conrath E, Berthod P. Microstructure Evolution in Bulk and Surface States of Chromium rich Nickel based Cast Alloys Reinforced by Hafnium Carbides after Exposure to High Temperature Air. Materials at High Temperatures 2014; 31(3): 266-273. http://dx.doi.org/10.1179/1878641314Y.0000000023

[16] Conrath E, Berthod P. Microstructure Evolution at High Temperature of Chromium-rich Iron-based alloys Containing Hafnium Carbides. International Journal of Materials Research (Zeitschrift für Metallkunde) 2014; 105(8): 717-724. http://dx.doi.org/10.3139/146.111085

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