

ISSN(PRINT) : 2320 -1967 ISSN(ONLINE) : 2320 -1975



ORIGINAL ARTICLE

CHEMXPRESS 9(2), 225-233, (2016)

Microstructure and oxidation behavior at 1100°C of nickel-base alloys containing hafnium carbides

Patrice Berthod, Elodie Conrath

Institut Jean Lamour, Faculty of Sciences and Technologies, University of Lorraine, B.P. 70239, F-54506 Vandoeuvre-lès-Nancy, (FRANCE) E-mail: patrice.berthod@univ-lorraine.fr Received : 10th June, 2015 ; Revised : 02nd October, 2015 ; Accepted : 10th October, 2015

Abstract : Three nickel-base alloys containing 25wt.% Cr, 0.25 to 0.50wt.% C and Hf contents high enough to obtain significant hafnium carbides for achieving high strength at high temperature were elaborated by foundry then exposed at 1100°C for 46 hours. Afterwards they were observed in cross section and submitted to indentation tests. Interdendritic HfC carbides were successfully obtained, alone for given Hf/C atomic percent ratio or with additional Cr carbides. The HfC volume fractions slightly decreased during the 1100°C stage while, inversely, chromium carbides grew a little.

INTRODUCTION

Since several decades ago there are increasing needs of metallic materials suitable at high temperature under significant mechanical stresses^[1,2] and in severely aggressive atmospheres^[3]. Cobalt-base, nickel-base and {iron, nickel}-base alloys were developed with increasing microstructure complexity. The nickel-base alloys family is maybe the most important one in the worlds of superalloys. Indeed many of the most modern alloys based on nickel bring exceptional mechanical^[4] and chemical^[5] resistances The room temperature hardness was lowered of 25-40Hv consecutively to the HfC fragmentation occurred during the 1100°C stage. The cross-sectional surface characterization showed that the three alloys well behaved in oxidation at 1100°C, with an external chromia scale and Cr content remained high in subsurface. © **Global Scientific Inc.**

Keywords : Ni-base superalloy; HfC carbides; High temperature; Microstructure; Hardness; Oxidation.

at elevated temperatures, despite the melting point of their base element which is several tens degrees lower than cobalt and iron^[6]. This is notably the case of the single-crystal nickel-base superalloys which are totally free of any weakening grain boundaries and the heat treatments of which may lead to precipitation of γ' (gamma prime) reinforcing intermetallic particles in great proportions. Unfortunately such high performance alloys cannot contain chromium in levels high enough to allow them resisting corrosion by melts (liquid sulfate, glasses, CMAS...) for which aluminum is much less efficient than for

226

resisting dry oxidation. The sufficiently high chromium contents required in such cases do not allow the strengthening by the gamma prime intermetallics. Other metallurgic means must be then applied. Oxide Dispersion Strengthened alloys may be a solution but they are generally devoted to pieces with elongated or plane shapes while alloys based on very refractory elements (tantalum, tungsten...), which may be fabricated in complex shapes by powder metallurgy necessarily lead to high densities no suitable for many applications. The reinforcement by carbides, although a rather old solution, which can be achieved in alloys obtained by casting, may be a solution.

Carbides reinforcing cast equiaxed alloys in hot applications must be stable enough at high temperature to maintain the mechanical properties on long time. At temperatures higher than a thousand degrees, for example 1100°C (which is the temperature limit of the single-crystal nickel-base alloys because of the dissolution of their reinforcing intermetallic particles at this temperature), chromium carbides rapidly decrease in volume fraction while much more stable carbides such as the TaC ones, know a beginning of fragmentation phenomenon. Other MC carbides, the HfC ones recently discovered as being better in this field^[7, 8], presented better thermal stability than TaC. Unfortunately the concerned cobaltbase alloys were not resistant enough against oxidation, principally because of the intrinsic oxidation behavior of cobalt-base alloys (too slow Cr diffusion). Such behavior may be of course improved by increasing the alloys' chromium content but such Cr enrichment generally favors in cobalt alloys the appearance of brittle sigma phases. In contrast nickelbase alloys, with their significantly better general oxidation behavior for Cr contents not too high, may present a good compromise between high temperature oxidation resistance and sufficient mechanical properties (such as creep-resistance), if the HfC carbides first well formed at solidification and remain stable enough (in terms of volume fraction and morphology) at the service temperature. Notably the second point must be verified since some MC carbides - as the TaC ones - which appear in cast cobaltbase^[9] and iron-base^[10, 11] alloys during their solidification and which are rather stable at high temperature, are not so able to appear in nickel-base alloys and the obtained ones rapidly disappear during high temperature exposures^[12].

The purpose of this work is to solidify three molten nickel-chromium alloys containing carbon and hafnium high enough to favor the formation of HfC carbides, in order to verify whether they really form, and thereafter to observe their behavior at an elevated temperature as high as 1100°C. By performing the high temperature exposure tests in air the posttest observation of the samples' surface will additionally give first information about the oxidation behavior of such alloys.

EXPERIMENTAL METHOD

Elaboration of the alloys

Three alloys, prepared by targeting the compositions given in TABLE 1, were elaborated using an induction furnace (CELES) working at medium frequency (110-120 kHz). Parts of pure elements (Alfa Aesar, purity > 99.9 wt.%) were weighed (microbalance, precision: 0.1mg) to constitute mixes of about 40g. Each mix was put in a water-cooled copper crucible surrounded by a water-cooled copper coil. A silica tube was inserted between the crucible and the coil, and a 300 millibars argon atmosphere was created inside.

The mix was heated until reaching 4kV for the generator, with an intermediate stage at 2500V for allowing an intermediate temperature homogenization before final heating to fusion. The heating of the molten alloy was maintained at about 1500-1600°C by applying a constant voltage of 4kV during about three minutes, for ensure that all parts were really melted and that the liquid alloy get chemically homogenized. The decrease in applied power induced the solidification and the cooling of the obtained ingot.

High temperature exposure runs

After return to room temperature and exiting out of the furnace each ingot was cut with a metallography saw into several parts. A first one was reserved for metallographic examination of the as-cast mi-

Names given to the alloys - Weight contents (%)	NiHfC1-1	NiHfC2-1	NiHfC2-2
Ni	BAL.	BAL.	BAL.
С	0.25	0.50	0.50
Cr	25	25	25
Hf	37	37	5.6

TABLE 1 : Targeted chemical compositions of the studied alloys (in weight percent)



Figure 1 : General view of the NiHfC1-1 microstructure (top) and enlargement of the central part (bottom); SEM/BES micrographs

crostructure and a second one was conditioned for the high temperature tests.

Since some information about the oxidation behavior was also expected a special surface state was realized for the samples. These ones, with approximate dimensions $9 \text{ mm} \times 9 \text{ mm} \times 3 \text{ mm}$ after cutting, were ground with a 1200-grit SiC paper on their six faces, while their edges and corners were smoothed with the same paper to prevent any too fast oxidation locally and help the formed oxide scales to re-



Figure 2 : General view of the NiHfC2-1 microstructure (top) and enlargement of the central part (bottom); SEM/BES micrographs

main on the substrates along the cooling.

The oxidation runs were performed in a 1.5L/h flow of dry synthetic air through a tubular resistive furnace. After a heating at $+20^{\circ}$ C/min from room temperature, a 46 hours-long stage at 1100°C was realized. The rate of the cooling was of 5°C/min only to favor the conservation of the formed oxide scales on surface.

The oxidized samples were then all around covered by nickel electrolytic deposition (1.6A/dm²

during 2 hours in a Watt's bath maintained at 50°C) after a preliminary gold cathodic deposition to get an electrically outer surface. The obtained nickel shell was thick enough to prevent any loss of the external oxide scale (more precisely the parts of it not loosed during cooling by spallation) during their cutting in two parts.

Metallographic characterization

As the ingots previously, the electrolytically coated oxidized samples were cut using a Delta Buelher saw. The two halves were embedded in a cold resin mixture (resin CY230 and hardener HY956 from ESCIL, France), then ground with SiC papers, for grade varying from 80 to 4000. After their cleaning using ultrasonic vibrations in ethanol, they were polished with a textile disk enriched in 1 μ m alumina particles to obtain a mirror-like state. The as-cast parts were subjected to the same preparation.

The microstructures of the as-cast samples and the ones aged at 1100°C were observed by Scanning Electron Microscopy (SEM, JEOL JSM-6010A) in Back scattered Electrons Shadow image (BES). The general chemical composition of the alloys was controlled by Energy Dispersion Spectrometry (EDS) using the EDS device equipping the SEM. Spot EDS measurements were additionally carried out to specify the chemical compositions of the present phases. The carbides phases were subjected to the measurement of their surface fractions using the Image Analysis tool of the Adobe Photoshop software.

The oxidized states were also characterized in cross-section by the observation and the chemical analysis of the different externally and internally formed oxides. EDS measurements were also performed in the outermost parts of the alloys to know the new local contents in chromium and hafnium.

RESULTS

Microstructures of the as-cast alloys

As demonstrated by the SEM/BES micrographs in Figure 1. (NiHfC1-1), Figure 2. (NiHfC2-1) and Figure 3. (NiHfC2-2), HfC carbides were successfully obtained in these nickel-chromium base alloys. HfC are the only carbides present in the NiHfC1-1 alloy. The matrix (grey in BES mode) is austenitic and dendritic, and all the HfC carbides (white in BES mode) are located in the interdendritic spaces. Their script-like shape evocates a eutectic {matrix+HfC} compound appeared at the end of solidification as suggested by its location. One can notice that, despite the rather low carbon content in this alloy (0.25 wt.%C) the HfC carbides are present in significant quantity.

The microstructure of the NiHfC2-1 alloy, displayed in Figure 2. with two magnifications too for having a general view as well as more details in the central part, is also dendritic. It contains two types of carbide: mainly HfC carbides (white in BES) and also chromium carbides (grey darker than matrix, almost black with the applied contrast and brightness). As for the previous alloy the HfC carbides are interdendritic elongated or script-like carbides. The chromium carbides, also located in the interdendritic spaces are less numerous but coarser. Despite their greater size it was not possible to clearly specify the nature of these chromium carbides $(Cr_7C_3 \text{ or } Cr_{23}C_6)$ neither by EDS spot analysis nor by microprobe, but one can think that they are probably $Cr_{7}C_{3}$. Thanks to its double content in carbon by comparison to the first alloy, the carbide population (HfC + chromium carbides) is denser, and consequently the microstructure seems to be a little finer.

The third alloy (NiHfC2-2) has the same dendritic and rather fine microstructure as the later alloy, but the HfC carbides are more present while rare chromium carbides also exist. Consequently to the higher density of the HfC carbides in this third alloy, these ones seem to be almost interconnected along the interdendritic boundaries.

Microstructures of the aged alloys

After 46 hours spent at 1100°C the microstructures of the three alloys have a little evolved, as illustrated in Figure 4. Indeed, the quantities of the HfC carbides and of the chromium carbides are qualitatively not changed, even it seems that there is a little more chromium carbides in the three alloys.



Figure 3 : General view of the NiHfC2-2 microstructure (top) and enlargement of the central part (bottom); SEM/BES micrographs

Notably, some rare chromium carbides are present in the first alloy which did not contain this type of carbide in its as-cast condition. The HfC carbides seem to have get a little fragmented during the high temperature stage, phenomenon visible in the three alloys.

To more accurately specify the possible surface fraction evolutions of the carbides image analysis was performed. Three results were obtained on $\{\times 1000\}$ SEM/BES pictures (i.e. the top micrographs in Figure 1 to 3) per alloy. The calculated average and standard deviation values are graphically presented in Figure 5. These quantitative results allow seeing that there are effectively more chromium carbides in each of the three alloys, and also that the surface fraction of the HfC carbides has itself a little evolved (decreased notably in the case of the NiHfC2-2 alloy).

Additional EDS spot analysis were performed in the matrix in order to reveal possible evolution in the contents in chromium and hafnium, the two elements involved in the two types of carbides the quantities of which have varied. The results (average value and standard deviation from four spot analysis in each case) are graphically displayed in Figure 6. The chromium content has obviously really varied in the matrix of the two carbon richest alloys, NiHfC2-1 and NiHfC2-2, with a decrease of



Figure 4 : Microstructures of the three alloys after 46 hours at 1100°C; SEM/BES micrographs



Figure 5 : Image analysis results obtained for the surface fractions of the HfC carbides and of the chromium carbides in the as-cast alloys and in the aged alloys



more than 1 wt.% which is at least qualitatively in accordance with the precipitation of supplementary chromium carbide phase as evocated above. In contrast, one cannot say that the already very low Hf contents in matrix have really varied. Indeed, the results for a same alloy for the same condition (ascast or aged) are rather scattered, as proved by the very high standard deviation values (of the same order of magnitude as the average value itself). Such variations for hafnium may be attributed to the high density in carbides and fine microstructures which may lead to a high probability of the volume or depth affected by the electron beam and subjacent hafnium carbides.



Figure 7 : Influences of the C and Hf contents and of the as-cast or aged state of the measured hardness

for the 0.25wt.%C-containing one and, among the two formers, higher for the Hf-richest alloy than for the Hf-poorer one.

Oxidation behavior

The surface states as appearing in cross-section are illustrated in Figure 8. It seems that an outer chromium oxide formed over the alloys' surfaces in all cases. This external chromia layer was probably compact and continuous but it was obviously deteriorated by the cooling, the thermal contraction mismatch between the oxide and the metallic substrate induced oxide spallation. Nevertheless the parts still present on surface and protected by the electrolytic nickel deposit during cutting allowed the characterization of the oxides. The scales were thus essen-



Figure 8 : Surface states of the alloys after the exposures at 1100°C in air

Indentation results

Vickers indentation under a 30kg load was performed three times on the middle of each cross-section. The obtained results (average value and standard deviation) are presented in a graph in Figure 7. One can see that the aging at 1100°C induced a significant decrease in hardness, of several tens Vickers points, for the three alloys. It seems that, in both states (as-cast and aged), the hardness is dependent on the carbon content and on the hafnium content: it is higher for the 0.50wt.%C-containing alloys than tially chromia but some islands of white oxide rich in Hf as qualitatively shown by EDS spot analysis (probably HfO2 but oxides too small to be quantitatively specified) are also present. Some internal oxides were also detected by EDS here and there in the subsurface but many of the white particles present close to the surface are hafnium carbides: no carbide-free zone developed from the oxide/alloy interface, contrarily to other carbides-reinforced cast alloys.

The contents in chromium in the subsurface very



Cr and Hf weight contents (%) in the extreme surface

Figure 9 : Chromium and hafnium contents in the alloy sub-surface close to the oxidation front

close to the oxidation front (and also in hafnium) were measured by EDS spot analysis again. The results (Figure 9.) showed that the chromium contents have decreased (several weight percent) but not enough to start threatening the chromia-forming behavior of these alloys. The Hf contents is here too scattered, consequences of the presence of possible Hf carbides and Hf oxides in the neighborhood of the electron beam impact.

DISCUSSION

Differently to the much more common tantalum carbides (TaC) which are not stable in cast nickelbase alloys^[12] in contrast with cobalt-base alloys^[9] notably, the HfC carbides seem to be thermodynamically rather stable in the Ni alloys considered here. They appeared in great quantities at solidification and they remain rather stable at 1100°C even for the rather long duration of 46 hours. However a starting fragmentation was detected in the aged microstructures. The HfC carbides are approximately as fragmented as the TaC carbides in a cobalt-base alloys at 1100°C and as the HfC carbides in a cobalt-base alloy at 1200°C. Since tantalum carbides cannot obviously exist in nickel-base alloys^[12] such new MC carbides (HfC) may be very useful for achieving high and long lasting creep-resistance for cast chromium-rich alloys which are chosen to be based on nickel for oxidation resistance purpose. By comparison with similar 25wt.%Cr-containing cobalt alloys and even with the Hf-free versions of the later ones (which tend to oxidize catastrophically after short time^[3, 5, 8], for the same conditions of time, temperature and atmosphere, the resistance of the studied alloy to high temperature oxidation seems being much better: oxide scales made of compact chromia essentially, and limited loss in Cr content in extreme surface. This is almost the same chromia-forming behavior as binary Ni-25Cr or ternary Ni-25Cr-0.25 or 0.50C (in weight contents) known as very good in high temperature oxidation. It was logical to think that the presence of so high contents in hafnium, element reputed very oxidable, may lead to a deterioration of the general oxidation behavior of the alloys, even if the presence of hafnium in much more usual quantities (1 or 0.1 wt.% and less) is well known to be beneficial in this field.

The high hardness of the HfC carbides (about 3000Hv^[13]) led to values rather high for nickel-base alloys (200 Hv and more in the as-cast state). This was effectively clearly due to the HfC carbides since the hardness increases with the HfC surface fraction and decreased when these one decreased because of 1100°C aging. However such hardness values are still not at the level of the cobalt-base ones. This is favorable for machining easiness but this also maybe means that the mechanical resistance at high tem-

perature will be not at the same level as the similar cobalt-base alloys. This needs to be later examined.

CONCLUSIONS

The HfC carbides appeared here as an alternative to chromium carbides in the reinforcement of nickel-base alloys for high temperature applications. In contrast with the chromium carbides and even with the tantalum carbides, the HfC carbides - which appear without problem at solidification in nickel-base alloys - demonstrated a rather good stability at a so high temperature as 1100°C (temperature at which even the famous single crystal γ/γ 'superalloys are mechanically weakened because of the disappearance of their strengthening intermetallic precipitates) with as possible consequence honorable mechanical properties. This point remains to be later verified by mechanical tests at high temperature, in order to see whether the additional cost necessarily induced with the use of so high quantities of a so costly element may be justified.

ACKNOWLEDGMENTS

The authors wish thanking very much Mr. Thierry Schweitzer for his precious contribution in the preparation of the samples for the thermal tests.

REFERENCES

- C.T.Sims, W.C.Hagel; The Superalloys (John Wiley & Sons, New York), (1972).
- [2] E.F.Bradley; Superalloys: A Technical Guide (ASM International, Metals Park), (1988).
- [3] P.Kofstad; High temperature corrosion (Elsevier applied science, London), (1988).
- [4] M.J.Donachie, S.J.Donachie; Superalloys: A technical guide (ASM International, Materials Park), (2002).
- [5] D.J.Young; High temperature oxidation and corrosion (Elsevier Corrosion Series, Amsterdam), (2008).
- [6] P.T.B.Shaffer; Plenum press handbooks of hightemperature materials N°1.materials index (Plenum Press, New York), (1964).
- [7] P.Berthod; J.Alloys Compnds., 481, 726 (2009).
- [8] P.Berthod, E.Conrath; Mater.Chem.Phys., 143, 1139 (2014).
- [9] P.Berthod, S.Michon, L.Aranda, S.Mathieu, J.C.Gachon; Calphad, 27, 353 (2003).
- [10] P.Berthod, Y.Hamini, L.Aranda, L.Héricher; Calphad, **31**, 351 (**2007**).
- [11] P.Berthod, Y.Hamini, L.Héricher, L.Aranda; Calphad, **31**, 361 (2007).
- [12] P.Berthod, L.Aranda, C.Vébert, S.Michon; Calphad, 28, 159 (2004).
- [13] G.V.Samsonov; Plenum press handbooks of hightemperature materials N°2.properties index (Plenum Press, New York), (1964).