Hardness changes after a 1100°C annealing treatment applied to creep-resistant HfC-containing Co-based alloys for improving their machinability

Patrice Berthod, Elodie Conrath
Institut Jean Lamour (UMR 7198), Team 206 "Surface and Interface, Chemical Reactivity of Materials"
University of Lorraine, Faculty of Science and Technologies
B.P. 70239, 54506 Vandoeuvre-lès-Nancy, (FRANCE)
E-mail: Patrice.Berthod@univ-lorraine.fr

ABSTRACT

Mechanical strengthening by hafnium carbides is an innovative way for obtaining refractory alloys with superior creep resistance. The level of mechanical properties achieved at elevated temperatures is particularly high when the alloys are based on cobalt. Unfortunately the presence of HfC, notably in cobalt alloys which are rather hard compared with iron-based ferritic alloys and nickel-based austenitic ones, is prejudicial for the room temperature machinability of these HfC-strengthened Co-based superalloys. In this work, three cobalt-based superalloys containing hafnium carbides in several volume fractions, known for their exceptional resistance against high temperature creep, were elaborated and tested by Vickers indentation in their as-cast condition. In parallel two similar ternary cobalt-based alloys with the same contents in chromium and carbon were also elaborated and tested in hardness for specifying the effect of the presence of HfC carbides on the room temperature hardness. The alloys were also heated to 1100°C during 50 hours for modifying a little their carbides' volume fractions and morphologies in order to see whether such modifications may decrease a little their hardness. The obtained results show that this heat-treatment induced only little microstructure evolution but which was sufficient to lose up to 30 Vickers points, which may improve moderately the machinability of the alloys.
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INTRODUCTION

Except their possible used in cryogenic applications and at human body temperatures as prostheses, cobalt-based superalloys are essentially designed for high temperature applications involving mechanical stresses[1]. To present mechanical resistance high enough many of them contain carbides dispersed in their microstructures. Chromium carbides are the most often met ones in such alloys[2-4]. Other carbides are also often used: tantalum carbides, tungsten carbides…[1]. Among the MC-type

carbides also feature the HfC ones, which involves an element, hafnium, which is essentially an element known for its beneficial effect of the high temperature oxidation and corrosion behaviour of superalloys[5-6]. Recently the use of HfC carbides for high temperature mechanical purpose was envisaged for polycrystalline equi-axed cast chromium-rich cobalt-based superalloys[7-8]. It was demonstrated in a very recent work that these carbides, when present in quantity high enough, allowed cobalt-based superalloys resisting very efficiently against high temperature flexural creep deformation[9]. However, the high hardness of HfC carbides (2913 Hv_{50g} [10] by comparison the chromium carbides in general: 1650 Hv_{50g} for $Cr_{23}C_6$ or 1336 Hv_{50g} for Cr_7C_3), may be a cause of a more severe lack of machinability for cobalt alloys the hardness of which is already rather high before any addition of HfC.

Thinking that it is possible to soften such HfC-strengthened cobalt-based alloys by applying a heat treatment at high temperature, several alloys of this type were elaborated and isothermally exposed at high temperature for a significant duration, to study how hardness may evolve, and to see whether microstructure – notably the HfC carbides volume fraction and morphology – may change a little to facilitate machining without significant loss of the initial very good high temperature mechanical properties.

Experimental details

Three Co-25wt.%Cr alloys with various hafnium contents and carbon contents were cast under inert atmosphere (Ar, P=300mbar), using a High Frequency induction furnace (CELES, France). The targeted compositions were: Co-25Cr-0.25C-3.7Hf ("CHF1"), Co-25Cr-0.50C-3.7Hf ("CHF2A") and Co-25Cr-0.50C-7.4Hf ("CHF2B"). To better see how hafnium carbides may monitor hardness, two additional alloys with the same chromium and carbon contents, but free of hafnium, were cast in parallel, by following the same route: the ternary Co-25Cr-0.25C ("C1") and Co-25Cr-0.5C ("C2") alloys. All alloys were synthesized from pure elements (99.9wt.% of purity) and obtained as 40g-weighing ingots. Each of them was then cut in two parts: a one destined to the control of the as-cast microstructures (initial state), and another one devoted to high temperature exposure (aged state). The latter one was placed in the middle part of the furnace belonging to a SETARAM TG92 thermo-balance, in which it was subjected to a thermal cycle composed of a +20 K/min heating, a 50 hours stage at the constant temperature 1100°C, and of a -5K/min cooling down to room temperature. It was cut in to parts to allow the observation of the internal microstructure (far from the surfaces and subsurfaces affected by oxidation) as well as to perform indentations.

The as-cast parts and the aged parts were embedded in a cold resin mixture (ESCIL, France) and ground with SiC papers whose grade varied from 240-grit to 1200-grit. After ultrasonic cleaning final polishing was achieved using a textile disk enriched with fine hard particles until obtaining a mirror-like surface. The microstructures were examined using a JEOL JSM-6010LA Scanning Electron Microscope (SEM) in Back Scattered Electron mode (BSE), after having controlled the general composition of the alloys (except carbon) by Energy Dispersion Spectrometry (EDS). Image analysis measurement of the surface fractions of HfC carbides (supposed to be close to the volume fractions) was realized for the three HfC-strengthened alloys for their two states (as-cast and aged). EDS spot analysis was also carried out in their matrixes, for the two states again.

Each embedded and polished sample, as-cast or aged, was subjected to hardness evaluation. This was done according to the Vickers method (diamond pyramidal penetrator, load of 30kg progressively applied and maintained during 10 seconds), in three different locations. The average and standard deviation were calculated from these results for each alloy for its two states (as-cast and aged).

RESULTS AND DISCUSSION

As-cast microstructures

The microstructures of the five alloys just after their elaboration by foundry are illustrated in Figure 1 by SEM/BSE micrographs. In all cases the matrix is dendritic and the carbides are located in the interdendritic areas. The ones present in the ternary C1 and C2 alloys are exclusively chromium carbides (appearing darker than matrix in BSE mode) and these ones are logically more numerous in the
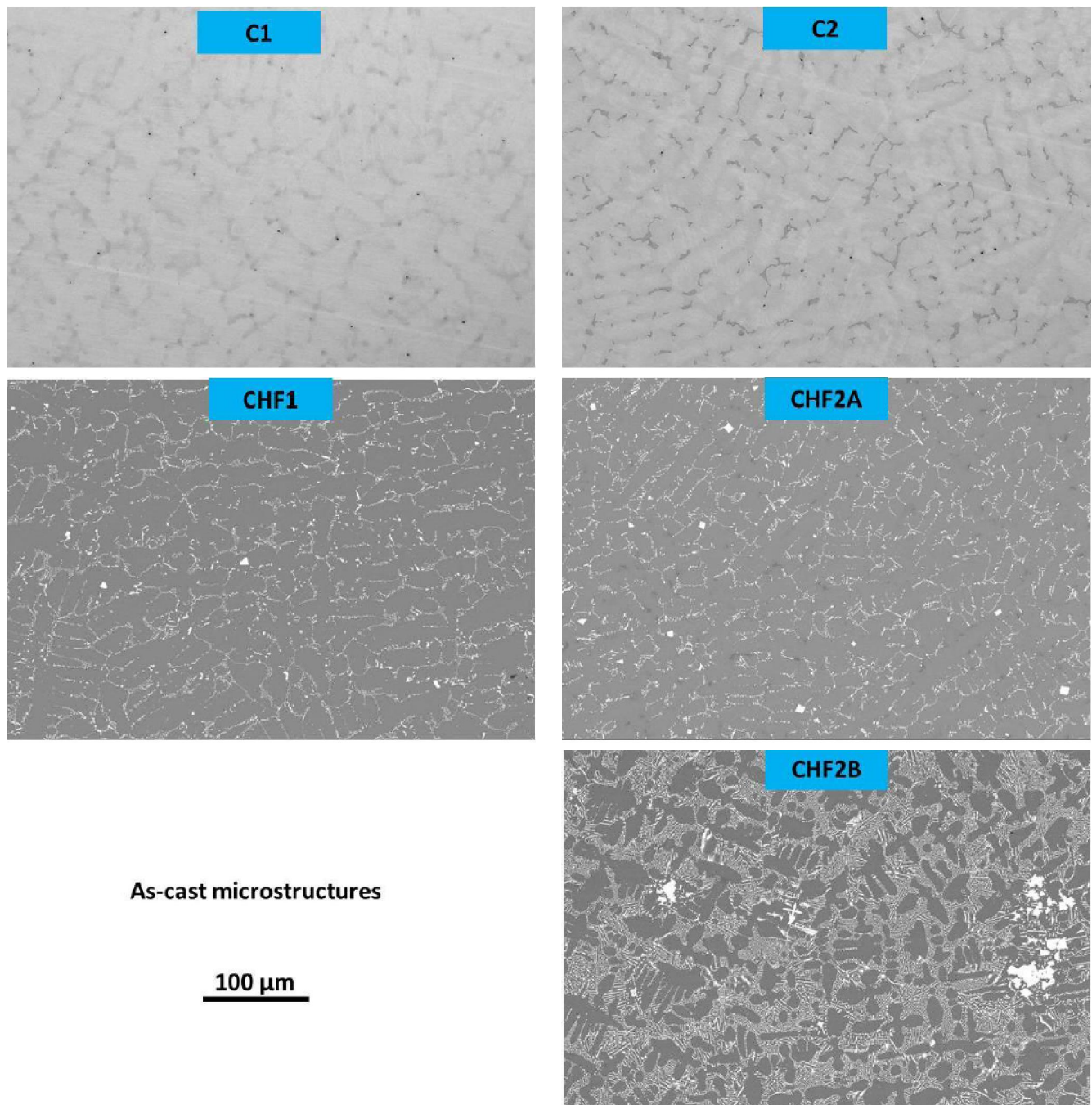
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Figure 1 : Microstructures of the five cobalt-based alloys just after their elaboration (SEM, BSE mode)

carbon-richest alloy (C2) than in the other alloy (C1). The carbides contained by the CHF1 and CHF2B alloys are only hafnium carbides (appearing in white in BSE mode). There are all interdendritic. Many of these HfC are script-shapes (forming a eutectic compound with matrix) but some of them are of a more compact morphology. These latter ones are probably pre-eutectic ones: precipitated in the molten alloy in the first instants of solidification.

As for C1 and C2, these carbides are much more present in the carbon-richest CHF2B alloy than in the CHF1 one. The fifth alloy, the CHF2A one, contains two types of carbides: HfC (blocky pre-eutectic and script-shaped eutectic) and chromium carbides. That ones are in minority by comparison with the hafnium carbides.

One can note that the obtained chemical composition of all these alloys (graphically presented in Figure 2 for Cr and Hf), specified with the EDS device equipping the SEM (average and standard
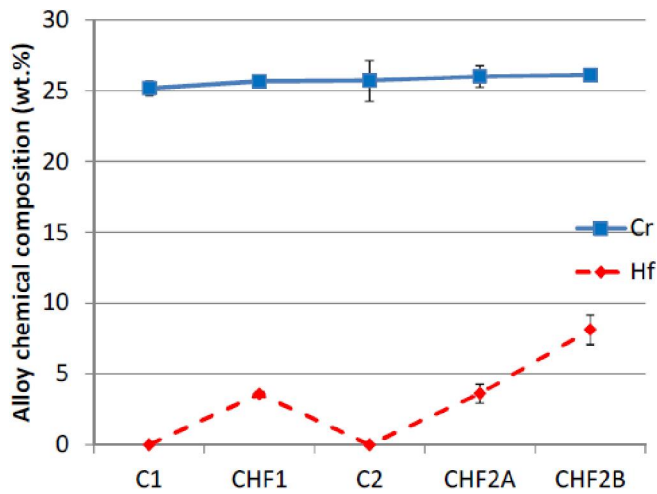
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Figure 2 : Chemical compositions obtained for the five alloys (except C not measurable)

Figure 3 : Illustration of the very good creep-resistance at elevated temperature of one of the HfC-strengthened alloys by the macrograph of a parallelepiped slightly deformed after a 100h-long 3-point central flexural creep test carried out at 1200°C for a 20 MPa resulting maximal tensile stress(office scanner)

deviation values calculated from three ×1000 areas), are in good accordance with what was targeted.

The microstructural principle exploited in these three alloys (strengthening by significant fraction in HfC carbides, notably interdendritic and script-shaped) led recently to exceptional behaviours in flexural creep in extreme conditions (1200°C, 20 MPa of resulting tensile stress in the bottom middle of 1mm × 2mm × 15mm parallelepipeds), as illustrated by the macrograph of the very slightly deformed sample (CHF2A alloy, 100h, 1200°C, 20MPa) in Figure 3. However this is accompanied by rather high value of hardness suggesting machining difficulties, the existence of which was confirmed during the preparation of the parallelepipeds devoted to the high temperature 3-points flexural creep tests[9].

Metallurgic state of the alloys after annealing at 1100°C for 50 hours

The as-cast microstructure states of alloys just after casting are generally not in equilibrium: present phase not chemically homogeneous (chemical segregations during solidification), precipitation of secondary phases not fully realized, accidental appearance of metastable phases… This is generally at the origin of particular transient properties such as too high hardness for example. Otherwise, because of the requirements of the phenomena involved in phase development during solidification (nucleation, growth…), the morphologies of secondary phases can be elongated (rods, plates…), shapes which led

to high interfacial energies stocked in the alloys. When exposed again at high temperature after these morphologies more or less evolve in order to minimize the Gibbs enthalpy of the whole alloy, by fragmentation, coarsening… which generally weaken it mechanically but which may also improve its machinability at room temperature. This is the reason why an annealing treatment was applied to the studied alloys, long enough (50 hours) but at a temperature elevated but not too high (1100°C), in order to preserve the essential strengthening for keeping the main part of the good mechanical properties at elevated temperature.

The microstructure modifications induced in the alloys by this heat treatment is illustrated in Figure 4, not only for the HfC-strengthened alloys but also for the ternary ones.

Globally the chromium carbides present in the ternary C1 and C2 alloys seem having coarsened, with an obvious increase in quantity. At this rather low magnification, the microstructure changes in the HfC-strengthened alloys seem inexistent in the CHF1 alloy, in contrast with the two other alloys in which more chromium carbides (dark) can be seen.

Observations at higher magnification give more details: the HfC carbides have almost not evolved, maybe except a slight increase in volume fraction (CHF1 alloy, Figure 5) but the chromium carbides are really much more numerous in the alloy in which some of them were already present in the as-cast state (CHF2A alloy, Figure 6) as well as in the CHF2B alloy which did not contain initially this type of carbides (Figure 7).
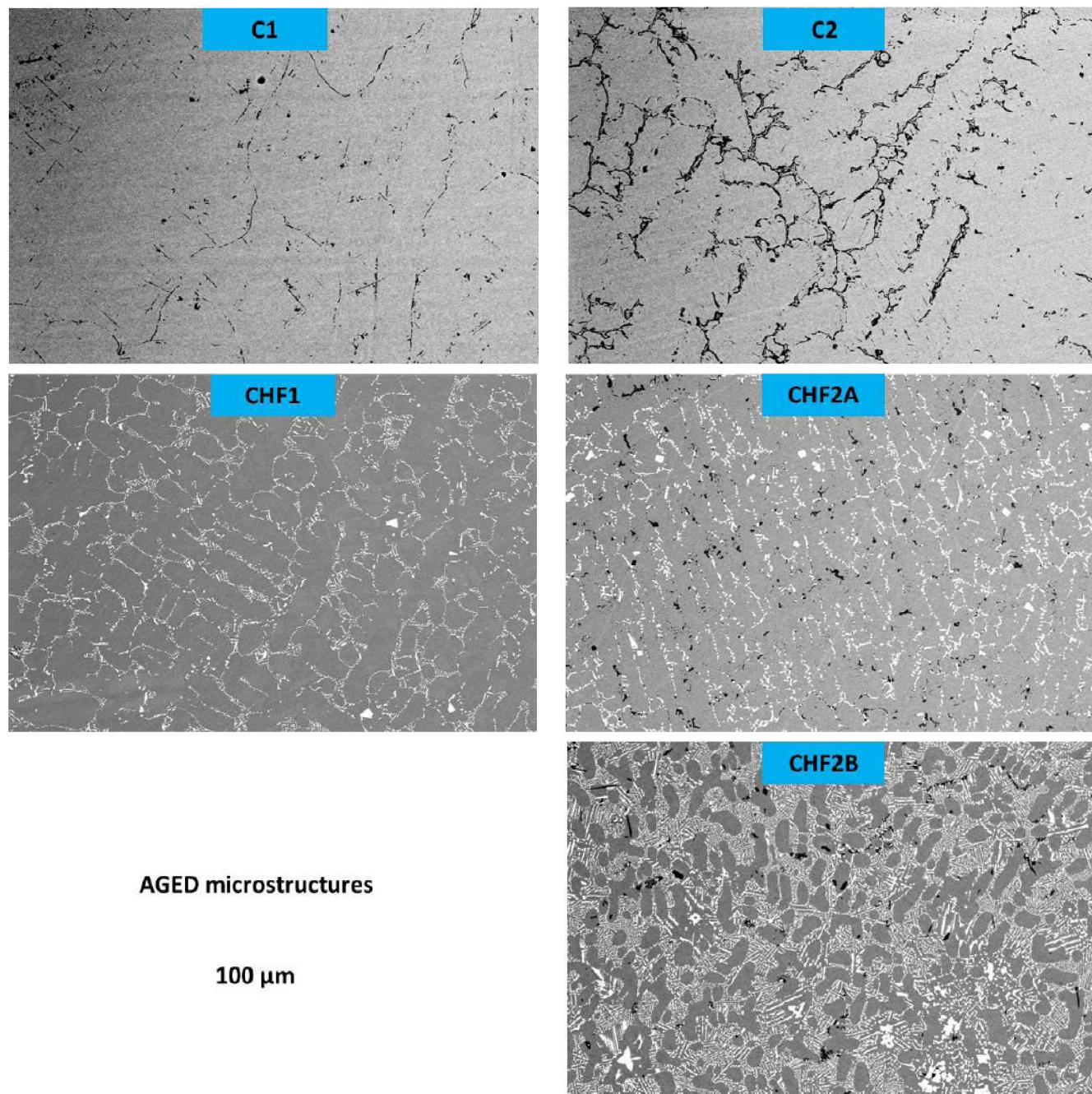
Figure 4 : Microstructures of the five cobalt-based alloys after {1100°C, 50h}-annealing (SEM, BSE mode)

These enlarged views confim that the microstructure evolution of the CHF1 alloy is very limited: the blocky shape of the pre-eutectic HfC carbides and the script shape of the eutectic HfC carbides are not noticeably modified. It is possible that these carbides are now a little thicker, this maybe resulting from an isothermal continuation of the growth from hafnium and carbon atoms having segregated in the interdendritic zones during solidification.

This can be also said about the HfC carbides of the CHF2A alloy. For this alloy the main change is the precipitation of many additional chromium carbides, of several sizes, which are maybe more Cr_7C_3 than $Cr_{23}C_6$ as suggested by their darker grey than the chromium carbides already present in the as-cast state.

Concerning the third HfC-strengthened alloy which initially contained numerous and coarse blocky pre-eutectic and script-shape eutectic carbides, no visible change concerning the hafnium carbides can be noticed. The main microstructure change is the significant appearance of chromium
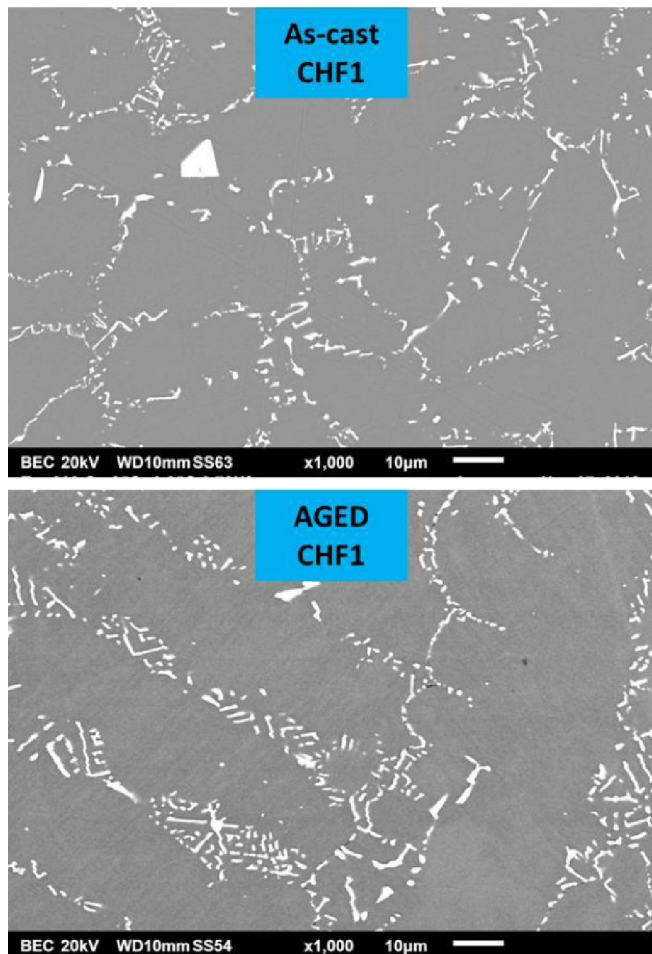
Figure 5 : Microstructure changes occurred during the annealing treatment, revealed by {as-cast ↔ annealed} comparisons at high magnification; case of the CHF1 alloy
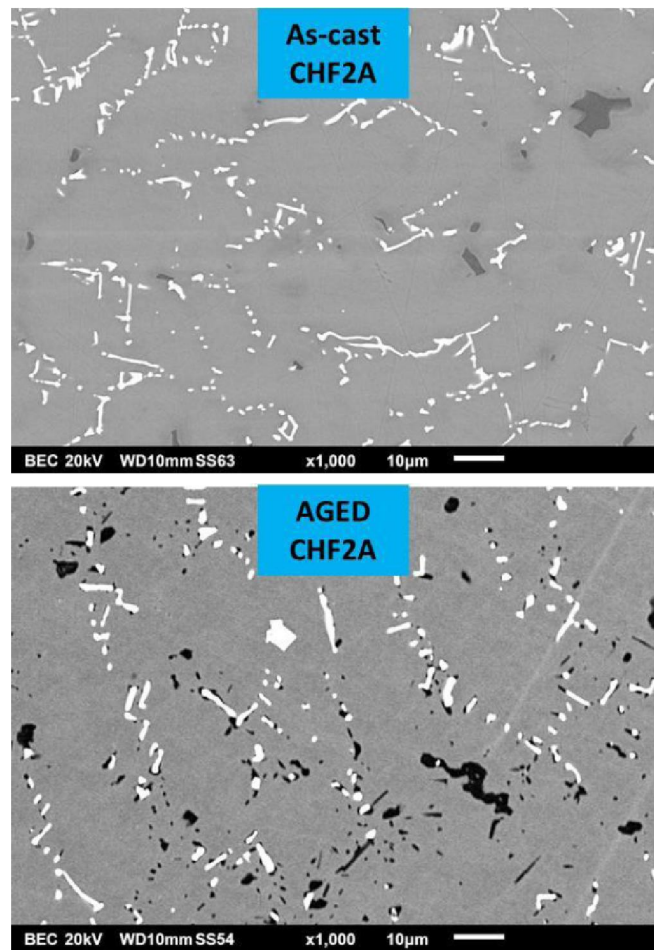

Figure 6 : Microstructure changes occurred during the annealing treatment, revealed by {as-cast ↔ annealed} comparisons at high magnification; case of the CHF2A alloy

carbides, although in much lower quantities than the hafnium carbides.

After these qualitative study of the microstructure changes induced by the annealing treatment in the the five alloys, some measurements were done for extending the metallographic characterization in a quantitative field. Image analysis was performed for each alloy and for the two states (as-cast and aged), on at least three ×1000 SEM/BSE micrographs. This led to the results graphically presented in Figure 8. One can see that, in fact, the HfC carbides did not evolve during the 50 hours at 1100°C for the CHF1 and the CHF2A alloys (the error bars are crossing), even if the average value seems being very slightly higher (CHF1 alloy) or very slightly lower (CHF2A alloy) after annealing. In contrast the surface fraction of HfC in the CHF2B alloy seems having decreased. However, here too, the error bars are crossing. In contrast the chromium carbides are

much more present in all the heat-treated alloys, except CHF1, as clearly seen in the micrographs.

The chemical composition of the matrix was analyzed by spot EDS measurements, and the average (points) and standard deviation (error bars) values are graphically presented in Figure 9. One can see first that the chromium content in matrix has generally increased during the annealing treatment, probable consequence of the carbides coarsening which let a little less space for matrix for a constant stocked chromium quantity (the chromium consumption by precipitation/coarsening of chromium carbides is generally very limited). Concerning hafnium, the initial level of Hf in solid solution was extremely low (and often null) in the as-cast state, and the not zero values may be attributed to possible intersection of the interaction peer under the beam with subjacent HfC carbides. However, the heat treatment led to a decrease in Hf content in matrix: some Hf atoms were probably
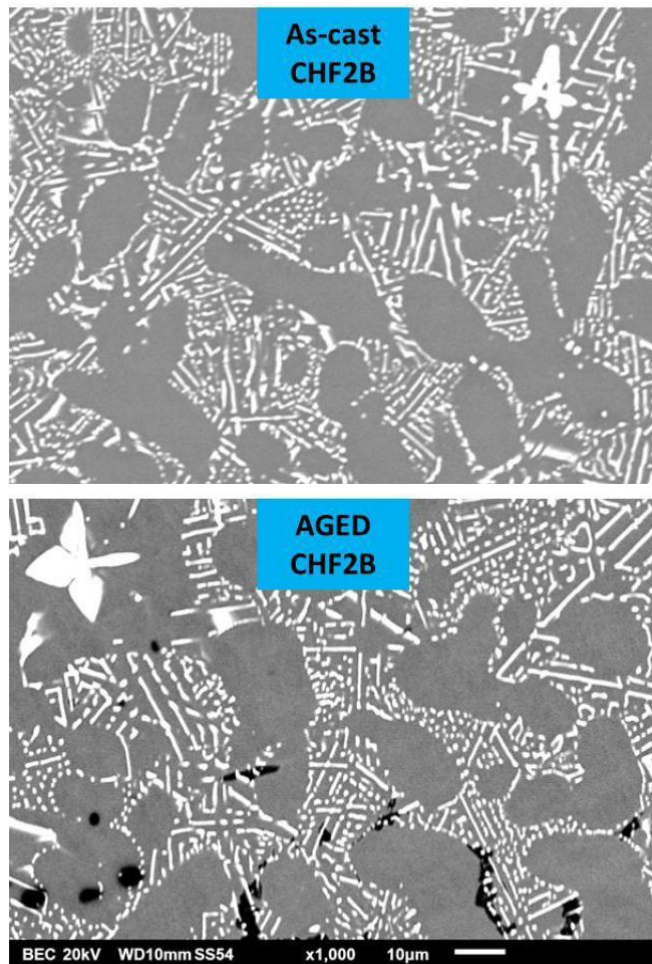
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Figure 7 : Microstructure changes occurred during the annealing treatment, revealed by {as-cast ↔ annealed} comparisons at high magnification; case of the CHF2B alloy
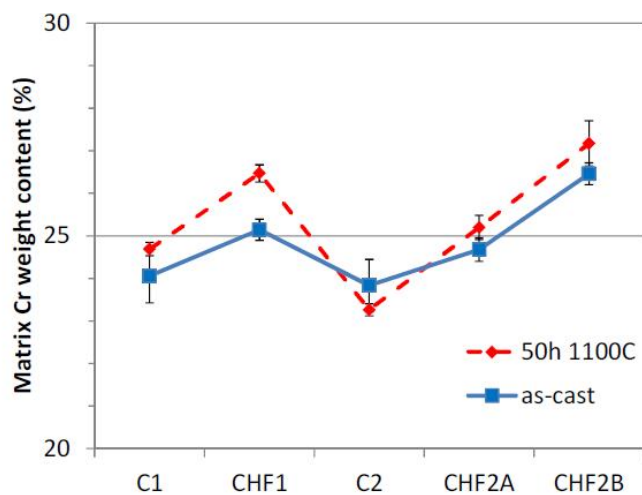

Figure 8 : Evolution of the surface fractions of the hafnium carbides (top) and of the chromium carbides (bottom) during the annealing treatment

Figure 9 : Evolution of the chemical composition of the matrix during the annealing treatment

trapped in the matrix by the too rapid solidification and the annealing treatment allowed them to precipitate HfC with carbon atoms (leading to the small increase in HfC surface fraction which was noted).
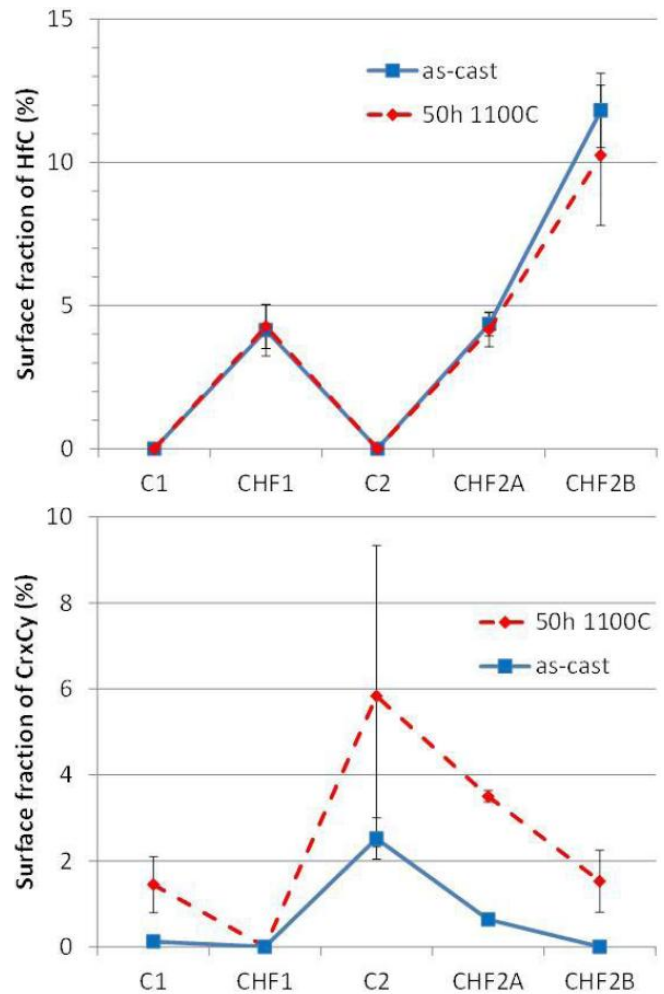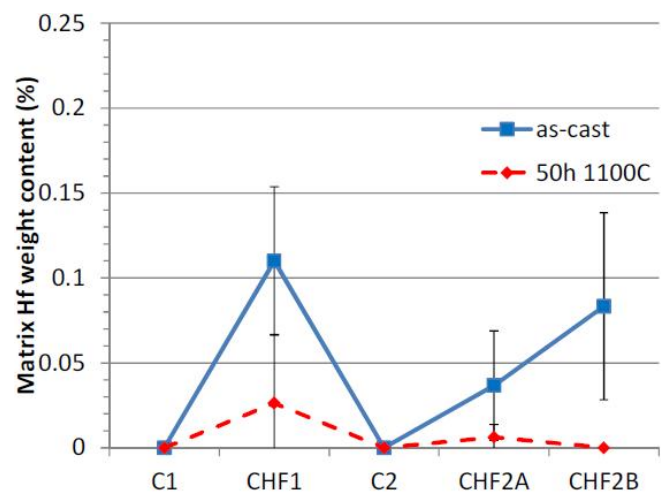
Hardness of the alloys after the annealing heat treatment

Three to five macro-indentations were carried out according to the Vickers method under a load of
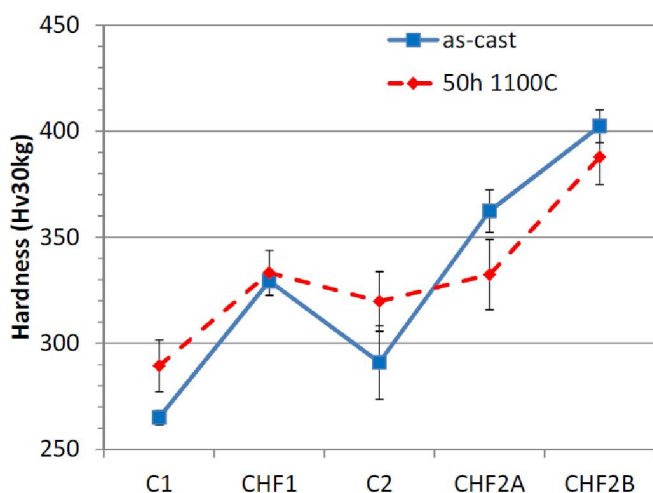
Figure 10 : Evolution of the hardness of the alloy during the annealing treatment

30kg, on the five alloys for their two metallurgical states. A decrease in hardness was effectively observed for the two 0.50C-containing HfC-strengthened alloys (CHF2A and CHF2B) but this one is rather moderate: 332 ±17 Hv_{30kg} against 362 ±10 Hv_{30kg} for the CHF2A alloy, and 388 ±13 Hv_{30kg} against 402 ±8 Hv_{30kg} for the CHF2B alloy. In contrast no significant difference was found in the case of the CHF1 alloy. Inversely, the hardness of the two ternary alloys has significantly increased: 289 ±12 Hv_{30kg} against 265 ±4 Hv_{30kg} for the C1 alloy, and 320 ±14 Hv_{30kg} against 291 ±17 Hv_{30kg} for the C2 alloy. This hardening in their case can be easily correlated to the increase in chromium carbide fraction observed in their heat-treated states. Although these two alloys became significantly harder they did not reach the high level of hardness of the three HfC-strengthened alloys.

CONCLUSIONS

The exceptional creep resistance of the cast cobalt-based alloys strengthened by hafnium carbides is due to the {interdendritic location + script shape/ mixing with matrix + high mechanical properties +

high thermal geometrical stability} combination brought by these carbides by regards with others. The last points of this combination, useful for high sustainability of high temperature components, are unfortunately detrimental for the machinability of pieces made from such alloys (high hardness) and – as it was seen in the present work – for their softening during a annealing treatment at 1100°C. Indeed, despite the rather long (and thus costly) duration of the applied annealing treatment, the hardness probably did not decrease enough to significantly facilitate machining. High performance cutting tools are thus required to machine such alloys and near-net shape casting can be a compulsory solution for limiting the removed matter before obtaining final shape and dimensions.

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