ISSN : 0974 - 7486 Volume 10 Issue 2

Materials Science

An Indian Journal

Full Paper

MSAIJ, 10(2), 2014 [72-78]

Metallographic characterization and indentation of two commercial cobalt-based superalloys synthesized with a fine microstructure

Adrien Frigério[1], Pierre-Yves Girardin[1], Patrice Berthod[2]*
[1]Lycée Henri Loritz, 29 Rue des Jardiniers 54000 Nancy, (FRANCE)
[2]Institut Jean Lamour (UMR CNRS 7198), department CP2S, team "Surface and Interface, Chemical Reactivity of Materials", University of Lorraine, B.P. 70239, 54506 Vandoeuvre-lès-Nancy, (FRANCE)
E-mail : patrice.berthod@univ-lorraine.fr

ABSTRACT

Two commercial chromium-rich cobalt-based cast superalloys belonging to the ones often considered for the hottest pieces of aero-engines were reproduced in laboratory scale by melting of pure elements under inert atmosphere and solidification of ingots of several tens grams. The as-cast microstructures were examined and specified using electron microscopy and energy dispersion spectrometry while the room temperature hardness was measured by Vickers indentation. The microstructures of the two alloys are especially fine and rich in carbides of several types: chromium carbides and MC-carbides, thanks to rather high carbon contents. Chromium, and eventually tungsten, was found in some of the coarse carbides while tantalum and tungsten obviously belonged to the elongated MC carbides. Titanium and zirconium, the two other MC-former elements were essentially found, in addition to Ta and W, in the blocky MC carbides existing besides the elongated ones. The Vickers macro-hardness at ambient temperature of the two alloys are all slightly higher than 400 HV.

KEYWORDS

Cobalt-based superalloys;
Commercial alloys;
Fine microstructure;
Hardness.

INTRODUCTION

An important family of polycrystalline superalloys is the carbides-strengthened cobalt-based superalloys one[1,2]. They are generally rich in chromium to be sufficiently resistant against high temperature oxidation and hot corrosion by developing a protective continuous layer of chromia over their surface[3,4], and their reinforcing carbides can be primary ones (formed during solidification and located in the interdendritic spaces) and/or secondary ones (precipitated in the matrix as fine homogeneously dispersed particles)[5]. The commercial alloys Mar-M 322 and Mar-M 509 are two examples of such superalloys based on cobalt and strengthened by carbides[6,7]. They are usually elaborated by foundry in great quantities and poured in moulds with rather great size to solidify with shapes of various pieces of aero-engines for example. This leads to rather coarse microstructures characterized by coarse grains favourable to a good resistance to creep deformation.

In the present work it was wished to explore the microstructures of such alloys when they are solidified much faster than in usual industrial conditions. Such rapid solidification was favoured by both a small size of ingot and by a metallic mould cooled by an external water circulation. The room temperature hardness was also specified to anticipate on the possible difficulties which may be encountered during machining.

EXPERIMENTAL

Compositions of the alloys of the study

The two alloys were synthesized by melting together the different elements belonging to the chemical compositions of the commercial alloys. Thus, for the first alloy, named “CoX”, pure cobalt, chromium, iron, carbon, tantalum, titanium, tungsten and zirconium were prepared with masses allowing obtaining an ingot of 40 grams and reaching the weight contents in these elements of the commercial Mar-M 322 cobalt-based superalloy. The chemical composition, as given in[7], is presented in the first line of TABLE 1. Similarly, the same pure elements, except iron replaced by nickel, were prepared by weighing in order to target the different contents listed in the first line of TABLE 2 for reproducing the Mar-M 509 industrial superalloy, as an ingot of about 40g again (alloy named “CoY”). Most of these elements were chosen with a purity higher than 99.9 wt.%, (Alfa Aesar).

Elaboration of the studied alloys

These different elements were put in the copper crucible of a CELES High Frequency induction furnace, following a procedure (mix) favouring a good homogenization of the liquid alloy during fusion. Heating of the mix of solid pure elements, fusion and high temperature dwell for homogenization of the liquid, and finally solidification and cooling were performed in 300 millibars of pure argon. Such inert atmosphere was absolutely necessary to prevent any oxidation of the ones among these numerous elements which are especially oxidable: Ti, Zr, Ta and W notably.

Metallographic preparation

The two ingots, both with a compact shape, were cut using an Abrasimet Delta cutter of Buehler. A part of such ingot was then embedded in a cold resin mixture (ESCIL: Araldite CY230 and hardener HY 956). The mounted samples were thereafter polished with SiC papers with grade from 120 or 240 up to 1200, under water. After ultrasonic clean the mounted samples underwent final polishing with a textile disk enriched in 1µm hard particles, until obtaining a mirror-like surface state.

Microstructure observations

The polished samples were examined using a JEOL JSM 6010LA Scanning Electron Microscope (SEM). Observations were done in Back Scattered Electrons (BSE) mode to with different magnifications mainly between ×250 and ×1000. The Energy Dispersive Spectrometry (EDS) device equipping the SEM was used to control the general chemical compositions of the alloys, to identify the observed precipitates and to specify the chemical composition of the matrix, both with pinpoint measurements. Additionally X maps were also acquired to better see the repartition of the different elements in the microstructure.

Macro-hardness measurements

The Vickers indentations were performed on the mounted samples by applying a load of 30 kg, using a Testwell Wolpert machine. Three indentations were realized and the three values of hardness led to an average value and a standard deviation one.

RESULTS AND DISCUSSION

Chemical compositions of the obtained alloys

The results of EDS analysis of the two synthesized alloys are given in TABLE 1 for the CoX alloy and in TABLE 2 for the CoY one, in the two cases in the second line of the table to make easy the comparison

TABLE 1 : Chemical composition of the CoX alloy (Mar-M 322: chemical composition of the commercial alloy as given in[7]; CoX: EDS analysis with the SEM on a × 1000 area); all contents given in weight percents

Alloys	Co	Cr	Fe	C	Ta	Ti	W	Zr	other
Mar-M 322	60.5	21.5	0.5	1.0	4.5	0.75	9	2	none
CoX ×1000	59.22	22.31	0.73	not meas.	4.92	0.66	10.65	1.50	/

TABLE 2 : Chemical composition of the CoY alloy (Mar-M 509: chemical composition of the commercial alloy as given in [7]; CoY: EDS analysis with the SEM on area with different magnifications) ; all contents given in weight percents

Alloys	Co	Cr	Ni	C	Ta	Ti	W	Zr	other
Mar-M 509	54.5	23.5	10	0.6	3.5	0.2	7	0.5	none
CoY ×1000	53.91	24.11	10.29	not meas.	4.04	0.04	7.36	0.25	/

with the targeted compositions.

The chemical composition of the CoX alloy is rather close to the Mar-M 322 commercial one, for the main elements as well as for the minor elements, despite the lack of accuracy of the EDS technique by comparison with the Wavelength Dispersion Spectrometry one (microprobes). This is also true for the CoY alloy, the chemical composition of which is also close to the Mar-M 509 commercial one.

Microstructure of the CoX alloy

The CoX alloy presents a dendritic microstructure and many interdendritic particles which are probably carbides (Figure 1, top), the great number of which per surface unit aera and cumulative apparent surface fractions result from the rather high carbon content (1 wt.%C) and the presence of several metallic elements with strong carbide-forming character (Ta, Ti, W, Cr...).

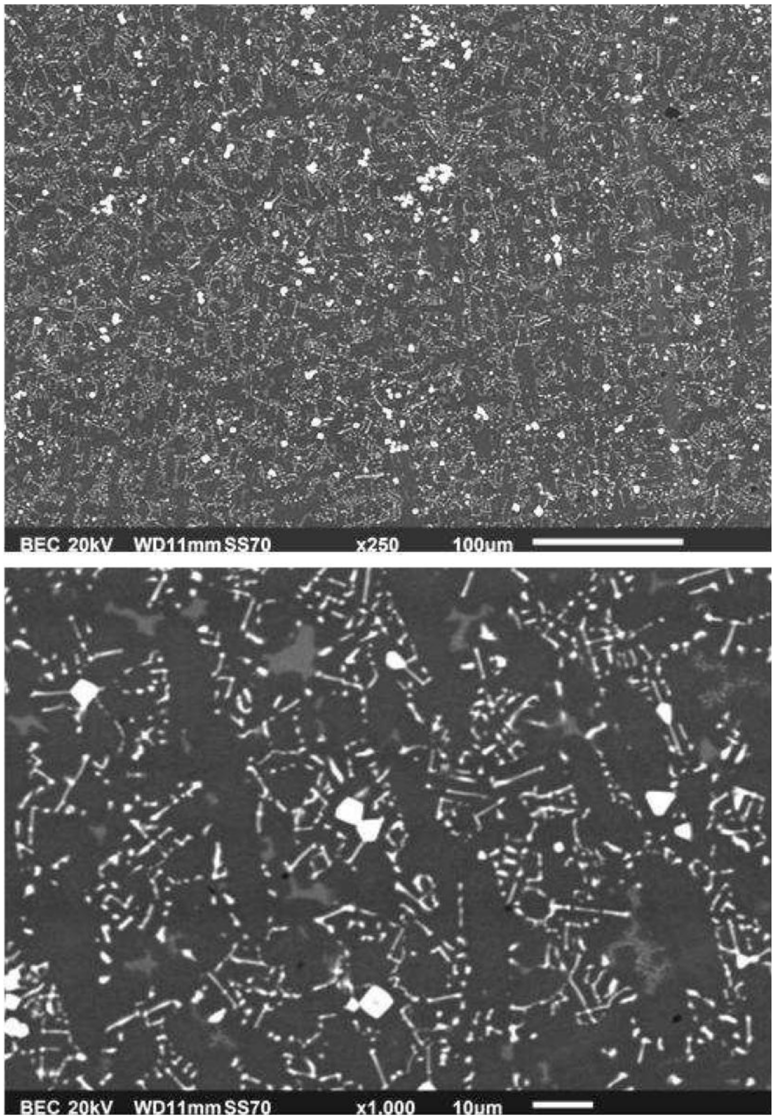

Figure 1 : Micrographs of the bulk microstructure of the CoX alloy in its as-cast condition at two magnifications (top: ×250, bottom: ×1000)

At higher magnification (Figure 1, bottom) the carbides seems being of essentially two types, appearing in white for most of them and in grey paler than the dark grey of the matrix. The white carbides are blocky for some of them (shape which let think that they perhaps formed in the early stage of solidification, simultaneously with the dendritic development or even before) and have more a script-like shape for all the others, typical of a carbide-matrix eutectic compound, formed at the end of solidification of the alloy. The grey particles are both less numerous and coarser.

EDS pinpoint analysis allows better specifying the particles (Figure 2). The white ones are effectively carbides, probably MC carbides more precisely. Indeed they contain on the one hand great quantities of Ta, Ti and Zr which are well-known to be MC-former elements, and on the other hand seemingly carbon in contents significantly higher than in matrix but which cannot be assessed by the EDS technique (too light element). The particles which appear paler than the previous carbides seem being also carbides. They are effectively richer in carbon than matrix (here too the real content cannot be quantified because of the limitations of the EDS technique) and especially rich in chromium as well as in tungsten.

They are probably carbides of both chromium and tungsten, but it is not possible to specify their stoichiometry by EDS. They seems to be not $(Cr,W)_{23}C_6$ since, on the one hand they do not have the same morphology ($M_{23}C_6$ are eutectic in such base of alloy), and on the other hand it is not probable that $M_{23}C_6$ may appear in an alloy with so high carbon content (1 wt.%). With a so high tungsten content, which explains the colour not darker (as many chromium carbides in a cobalt base alloy) but paler than matrix, it is possible that these pale particles would be M_6C carbides.

Microstructure of the CoY alloy

The CoY alloy also displays a dendritic cobalt-based matrix and many carbides (Figure 3). The darkest ones are seemingly eutectic chromium carbides: according to their morphologies, to the rather high carbon content in the alloy (0.6 wt.%C) and to the pinpoint EDS results (Figure 4), these ones are probably $(Cr,Co)_7C_3$ carbides. Besides these M_7C_3 carbides there are also white carbides which are without any doubt MC carbides since they are rich in more or less heavy MC-former elements: essentially Ta but also W and Ti.

As for the CoX alloy the EDS pinpoint measurements are not so really efficient in elongated carbides as in the more compact ones since the excitation volume involve not only these elongated carbides but also a part of matrix. X-Ray maps were performed for the alloys, as illustrated in Figure 5 in the case of the CoY alloy. One can see on these maps that:

- * matrix mainly contains cobalt, nickel and a part of chromium;
- * a great part of the latter element (Cr) is located were the dark carbides are present;
- * tantalum and tungsten are concentrated in the elongated white carbides;
- * the previous elements (Ta, W) are also present in the white blocky carbides but together with the two other MC-former elements titanium and zirconium.

Hardness of the CoX and CoY alloys

Several Vickers indentations were performed on the two mounted metallographic samples. The average value and the standard deviation are given in TABLE

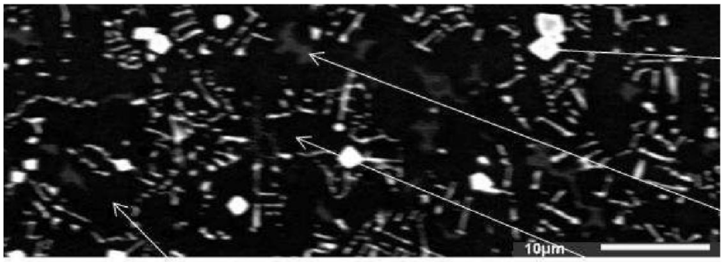

Figure 2 : EDS pinpoint analysis of the phases present in the CoX microstructure

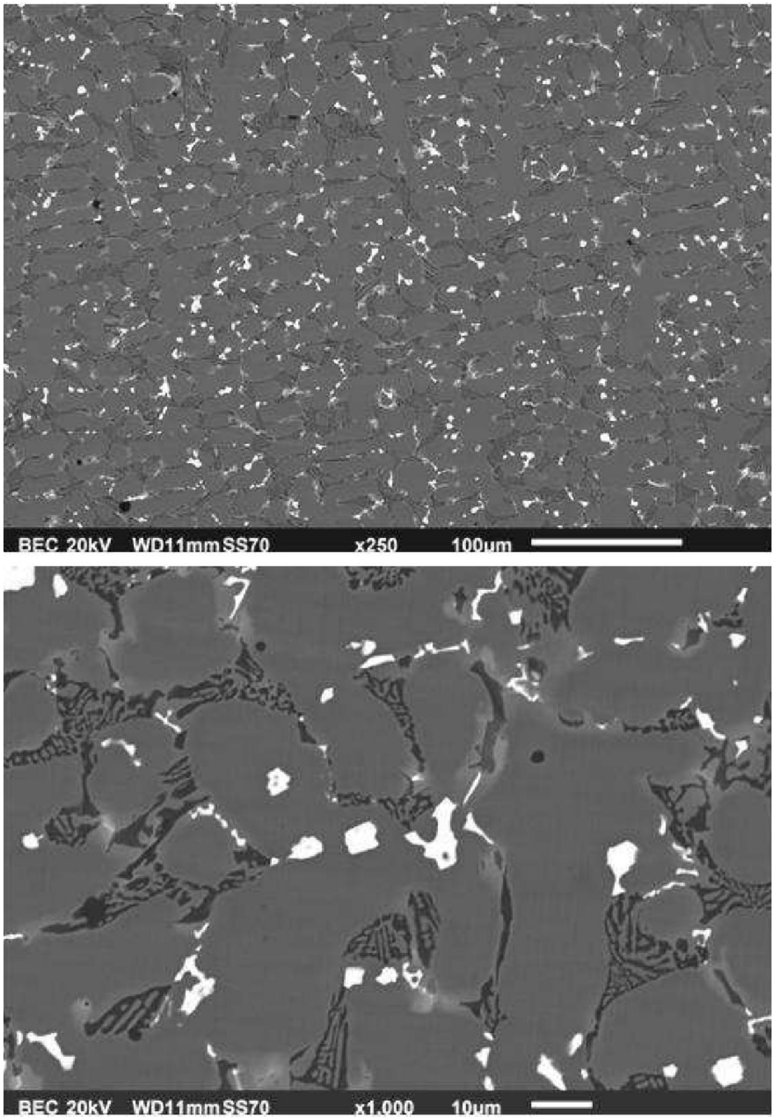

Figure 3 : Micrographs of the bulk microstructure of the CoY alloy in its as-cast condition at two magnifications (top: ×250, bottom: ×1000)

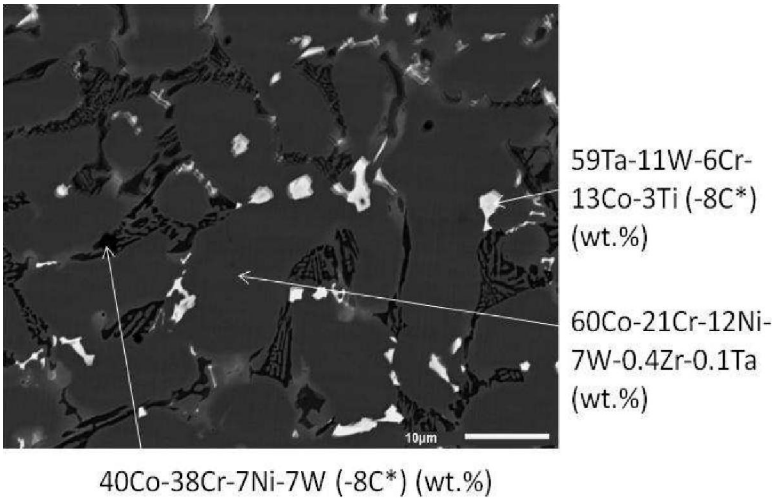

Figure 4 : EDS pinpoint analysis of the phases present in the CoY microstructure

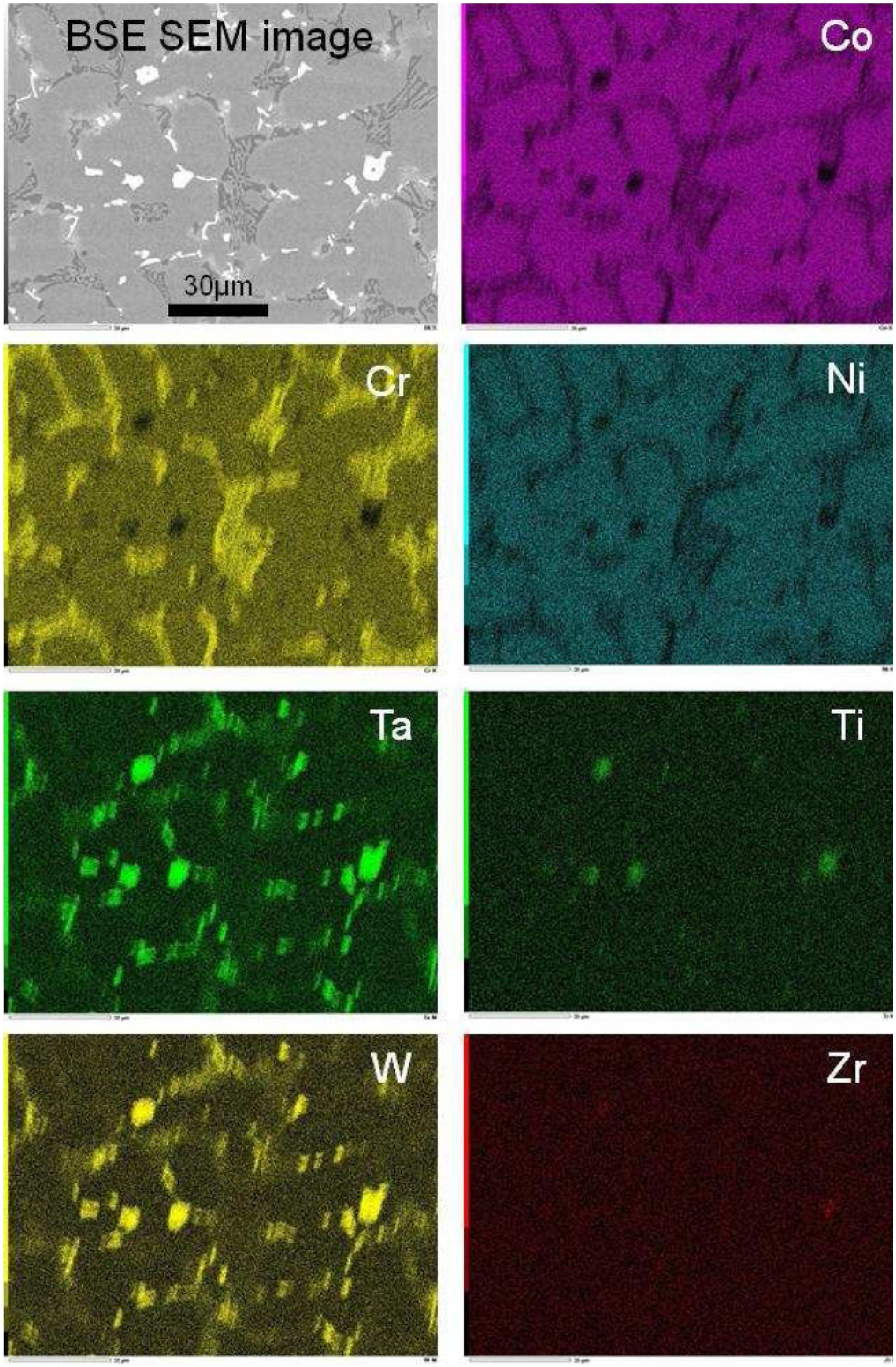

Figure 5 : X-Ray map acquired with the SEM and its EDS device on the CoY alloy

3. One can see that the hardness of both alloys is rather high. This can be attributed to the intrinsic high hardness of cobalt alloys on the first hand, and to the rather high density of carbides on the other hand. Indeed co-

balt alloys tend to be harder that nickel or iron alloys, and carbides are phases especially hard (more than one thousand Vickers[8]) by comparison to the metallic matrix. One can notice that the hardness of the carbon-richest alloy (CoX which contains 1 wt.%) is slightly higher than the one of the other alloy (CoY which contains 0.6 wt.%), the first one containing consequently more carbides than the second one, for, in the two cases, an especially high total content in strong carbides-former elements.

TABLE 3 : Vickers hardness of the two alloys (load 30 kg)

CoX alloy		CoY alloy	
Average value	**Standard deviation**	**Average value**	**Standard deviation**
423	± 20	404	± 16

General commentaries

In this special set of conditions of elaboration (laboratory-type synthesis from pure elements instead ferro-alloys for example), low weight of ingot and fast solidification, the obtained microstructures are rather interesting and several differences have appeared between the alloys industrially elaborated and the present alloys obtained in laboratory in small quantity. First the microstructure fineness is of course in opposite with the microstructure coarseness of the corresponding superalloys solidified as ingots of several kg or tens of kg. Second some of the phases may be not exactly the same, as for example the chromium carbides typically of the M_7C_3 type in the CoY alloy against the rather $M_{23}C_6$ often observed in the corresponding industrial superalloy.

Despite the finer microstructures which were obtained the hardness of these alloys in their as-cast condition is not very high and machining remains not very difficult to achieve. However, one noticed that the cutting of the ingots for preparing samples was not very easy to do.

Concerning the properties at high temperature the finer microstructure which were obtained here are probably less favourable for a good resistance against creep at high temperature, since it is generally considered that coarse microstructures are preferable for the mechanical resistance at high temperature[2,6,7]. The difference of fineness may also have consequences about the behaviour in oxidation at high temperature[9,10]. The consequences of the finer microstructures obtained on the properties of these alloys remain to be studied.

CONCLUSIONS

The laboratory reproduction of the two cast commercial superalloys of interest here, by melting pure elements together in order to get the original chemical compositions, was successful. Only small mismatches were found, essentially concerning the minor elements, and the microstructures obtained, analogous to the commercial alloys, were obtained in a finer version, with a room-temperature hardness still compatible with a not too difficult machining. The properties of these new alloys have to be later characterized, notably concerning the mechanical and chemical behaviours at high temperature.

REFERENCES

[1] J.M.Dorlot, J.P.Baïlon, J.Masounave; Des Matériaux, Editions de l'Ecole Polytechnique de Montréal, Montréal **(1986)**.
[2] C.T.Sims, W.J.Hagel; The Superalloys, John Wiley and Sons, New York, **(1972)**.
[3] P.Kofstad; High Temperature Corrosion, Elsevier applied science, London, **(1988)**.
[4] J.Young; High temperature oxidation and corrosion of metals, Elsevier, Amsterdam, **(2008)**.
[5] A.M.Beltram, C.T.Sims, N.S.Stoloff, W.C.Hagel; Superalloy II – High temperature materials for aerospace and industrial power, John Wiley, 135 **(1987)**.
[6] E.F.Bradley; Superalloys: A Technical Guide 1st Edition, ASM International, Metals Park, **(1988)**.
[7] M.J.Donachie, S.J.Donachie; Superalloys: A Technical Guide 2nd Edition, ASM International, Materials Park, **(2002)**.
[8] G.V. Samsonov; High-Temperature, Materials Properties Index, Plenum Press, New York, **(1964)**.
[9] P.Berthod, S.Raude, A.Chiaravalle, A.-S.Renck, C.Rapin, R.Podor; Revue de Métallurgie – CIT/ Science et Génie des Matériaux, **12**, 1031 **(2004)**.
[10] P.Berthod, S.Raude, A.-S.Renck, C.Rapin, R.Podor, P.Steinmetz; Materials Science Forum, **461-464**, 1173 **(2004)**.