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## Measurement of the densities of various cast refractory cobalt-based alloys; Influence of their chemical compositions and of the nature of the carbides if any

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### ABSTRACT

The volume mass of the refractory metallic alloys used in transportations, aeronautical and others, or for the hottest rotating tools in energy production or industrial processes, is frequently of importance due to the impact on energy economy and requirements in mechanical resistance. This is particularly true for superalloys, which are already rather dense and the density of which may be increased by the presence of strengthening heavy elements in solid solution or as dispersed particles of second phase. In this work several cast alloys belonging to the cobalt-based superalloys' family were subjected to the measurement of their densities. The obtained values were thereafter analysed by considering the base chemical composition and as well as the natures and fractions of the primary carbides ( $\text{Cr}_x\text{C}_y$ , TaC, HfC). The results show that the density variations between cobalt alloys, though rather limited, may be significant enough to have in some cases an importance in practice.

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### KEYWORDS

As-cast cobalt alloys;  
Density;  
Chromium carbides;  
Tantalum carbides;  
Hafnium carbides;  
Chromium content.

### INTRODUCTION

Chromium-rich cobalt-based alloys can be met in many applications, from cryogenic to ambient or body temperatures, as in prosthetic dentistry<sup>1</sup>, up to very high temperatures (e.g. turbine blades<sup>2</sup>, hot parts in industrial machines<sup>3</sup>), where one demands good corrosion resistance in corrosive aqueous solutions or against oxidation and corrosion by hot gases or molten salts/CMAS deposits<sup>4</sup>. Many of them contain carbon too, for allowing the development of car-

bides for achieving high mechanical resistance at high temperature (resisting creep deformation for example)<sup>5</sup>. Some versions particularly rich in carbon and highly alloyed with carbides-former elements can be considered to exploit the intrinsic high hardness of cobalt and the very high hardness of carbides, for applications such as cutting tools<sup>6</sup> (e.g. cobalt matrix hardened with high fractions of dispersed tungsten carbides), or for Co-W<sub>2</sub>C coatings<sup>7</sup> for preventing too fast wear of too soft metallic alloys. High densities of carbides may be met in al-

loys elaborated by foundry, as the very great fractions of chromium carbides earlier obtained in ternary chromium-rich cobalt-based alloys<sup>[8]</sup>.

Thus, notably the ones devoted to high temperature applications, many cast alloys may be considered as in situ composites materials combining a ductile and high toughness-presenting metallic matrix and significant amounts of hard strengthening carbides, the nature and volume fractions of which can be very variable alloy after alloy. These two main phases are generally of different volume masses which governs the global density of the whole alloys. Since this parameter is of importance for transportation uses (e.g. disks and turbine blades in aero-engines: for fuel economy) as well as in industrial processes (rotating tools: for lowering centrifugal mechanical stress), it is important to know the possible consequences of the strengthening metallurgical mean choice (type of carbide, its volume fraction, solid solution strengthening of matrix with heavy elements...) on the final density.

To start such analysis, here exclusively in the case of various chromium-rich cast cobalt-based alloys, one used, in this work, several geometrically well-defined samples, before future creep tests to what they were devoted. These ones were issued from the same ingots as other samples (for as-cast microstructure examinations, oxidation tests...) previously tested and characterized: {chromium carbides} - containing<sup>[9]</sup>, {tantalum carbides}-rich<sup>[10]</sup>, {hafnium carbides} – containing<sup>[9, 11, 12]</sup> and {Co-10Ni-30Cr}-based carbide-less or carbides-containing<sup>[13-15]</sup> alloys. Their densities were simply calculated from the volumes and masses of these samples, and the obtained results commented by regards to the chemical compositions and the microstructures.

## EXPERIMENTAL

Initially, all the alloys considered in the present work were earlier elaborated by foundry. This was done by melting together parts of pure elements (for most of them: Alfa Aesar, purity > 99.9wt.%) weighed with a microbalance (precision 0.1 mg) to target about 40g for the final ingot. The elaboration

apparatus was a CELES high frequency induction furnace (max. power: 50kW) operating with the following parameters: about 4kV and 110kHz. Heating, melting, stage in the liquid stage (duration 5 minutes) and cooling were done in a water-cooled copper crucible present in a chamber isolated from the laboratory air with a silica tube in which were 300mbars of pure argon prior to heating.

After cooling to room temperature the ingots were sawed with a Buelher Abrasimet Delta metallography cutter for parts destined to metallographic characterization, and either with a Buelher Isomet 5000 linear precision saw or a Struers Secotom-50 for obtaining elongated parallelepipeds (about 15mm-long, 2mm-width and 1mm-thick. The first ones were embedded in cold resin mixture (82% in mass of Araldite resin (CY230) and 18% in mass of hardener (HY256), ESCIL, France). Thereafter they were ground with SiC papers from 250-grit to 1200 grit under water as lubricant and cooling fluid, underwent ultrasonic cleaning, then polishing with textile disk sprayed by 1µm-alumina particles. Microstructure examinations were realized with a JEOL JSM 6010 LA Scanning Electron Microscope (SEM), with an acceleration voltage of 20kV, mainly in Back Scattered Electrons Composition mode (BEC).

The second ones were carefully polished (1200 SiC-paper and 1µm-textile) until obtaining almost perfect parallelepipeds, with wideness and thickness varying of only 0.01mm as maximum along them. Their dimensions were measured using an electronic calliper (precision 0.01mm). Their masses were measured using a precision balance ( $\pm 0.1$ mg). The density of each parallelepiped, more precisely its volume mass  $\rho$ , was then deduced by dividing the mass  $m$  by the volume  $V = L \times l \times e$ :

$$\rho = m / (L \times l \times e).$$

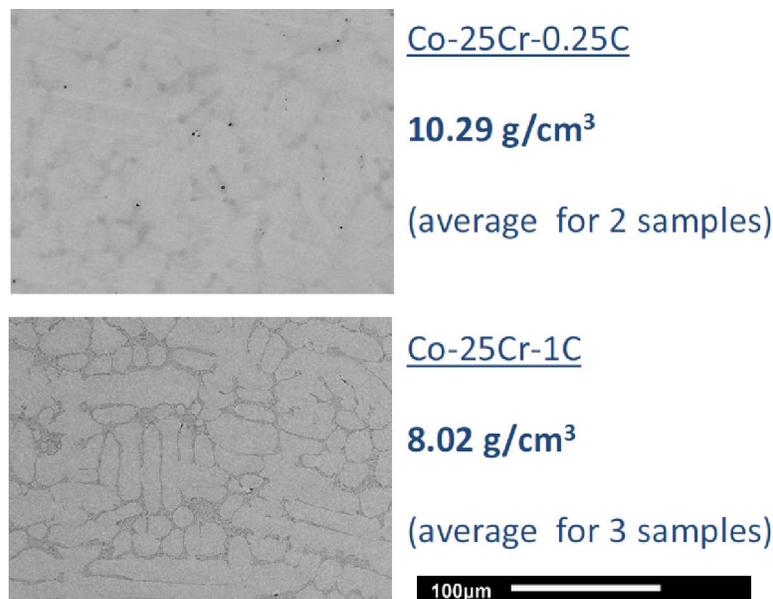
## RESULTS AND DISCUSSION

### As-cast microstructures and average density values

One or several (up to 4) parallelepipeds (example in Figure 1) were thus obtained for each of

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**Figure 1 :** Example of parallelepiped for density determination (scanned on all its four main faces using a Canon LiDE 210 office scanner)



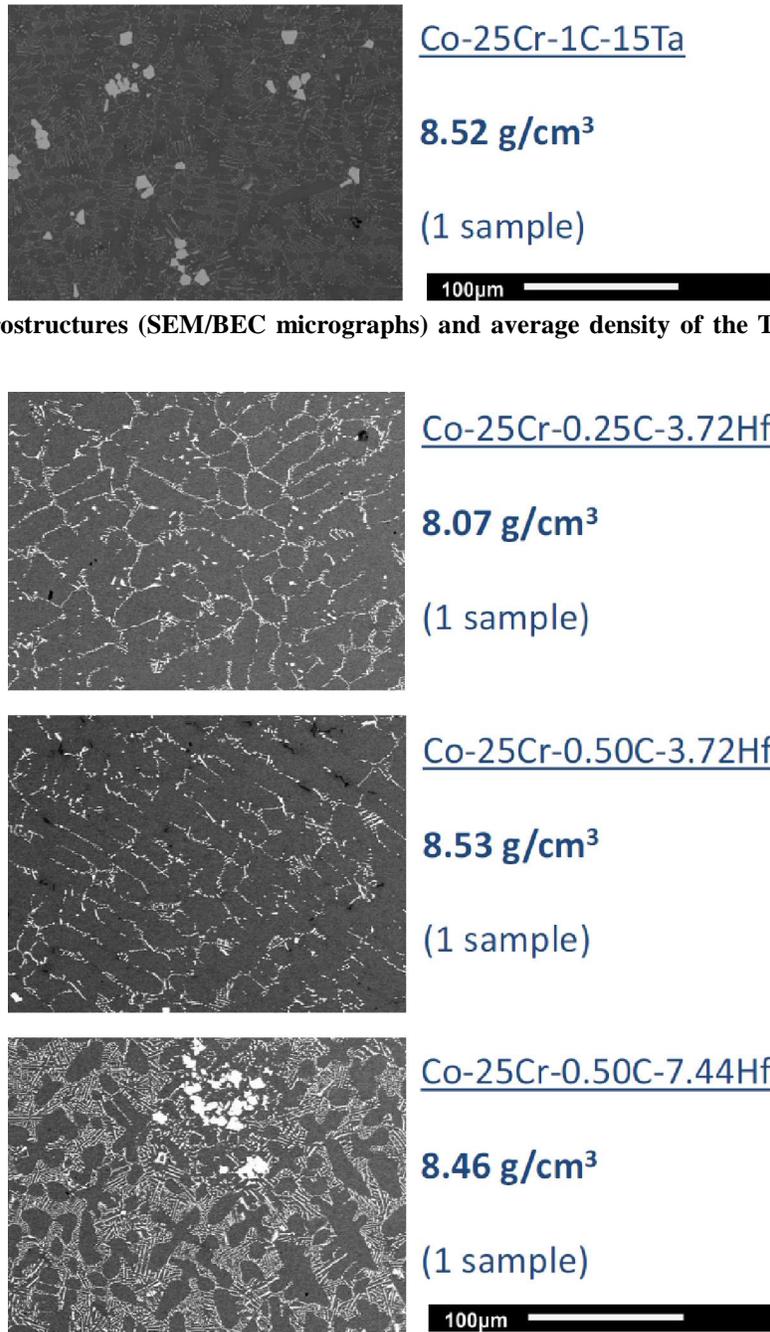
**Figure 2 :** As-cast microstructures (SEM/BEC micrographs) and average densities of the two ternary Co-25Cr-xC alloys

the eleven different cobalt alloys under study.

The first alloys subjected to the density determination are two ternary ones, Co(bal.)-25Cr-0.25C and Co(bal.)-25Cr-1.00C (contents in weight percent). Both of them present a dendritic cobalt matrix of solid solution in which some of the chromium and carbon atoms are dissolved, and interdendritic chromium carbides (grey particles darker than matrix, probably of the  $Cr_7C_3$  type) in low quantity in

the first alloy and in much higher quantity in the second one (Figure 2). The average volume masses, respectively of about 10.3 and 8.0 g/cm<sup>3</sup>, suggest that the carbide-richer alloy is significantly less dense than the other alloy.

The third alloy of this study is a quaternary one based on Co-25Cr and particularly rich in carbon (1wt.% C) and tantalum (15wt.% Ta). These unusually high Ta and C contents as well as the Ta/C atomic



**Figure 3 : As-cast microstructures (SEM/BEC micrographs) and average density of the TaC-rich quaternary Co-25Cr-1C-15Ta alloy**

**Figure 4 : As-cast microstructures (SEM/BEC micrographs) and average densities of several HfC-containing quaternary Co-25Cr-xC-yHf alloys**

ratio rated to 1 led to TaC exclusively (white particles), with a particularly high volume fraction (Figure 3). The obtained volume mass, about 8.5 g/cm<sup>3</sup>, is intermediate between the two former ones.

The three following alloys, which contain half the previous carbon content (e.i. 0.5 wt.%C against 1.0) and hafnium instead tantalum, are rich in HfC carbides (Figure 4). These hafnium carbides (white particles) are of two types, pre-eutectic ones (angu-

lar blocky compact) and eutectic ones (script-like, mixed with matrix in the interdendritic spaces). There are always very present in the 0.25C-3.72Hf alloy and in the 0.50C-3.72Hf one (which also contains dark chromium carbides), their surface/volume fraction is particularly high in the 0.50C-7.44Hf alloy. This is thanks to the Hf/C atomic ratio of 1 that the first and third alloys only contain HfC and no chromium carbide is present. The densities of these

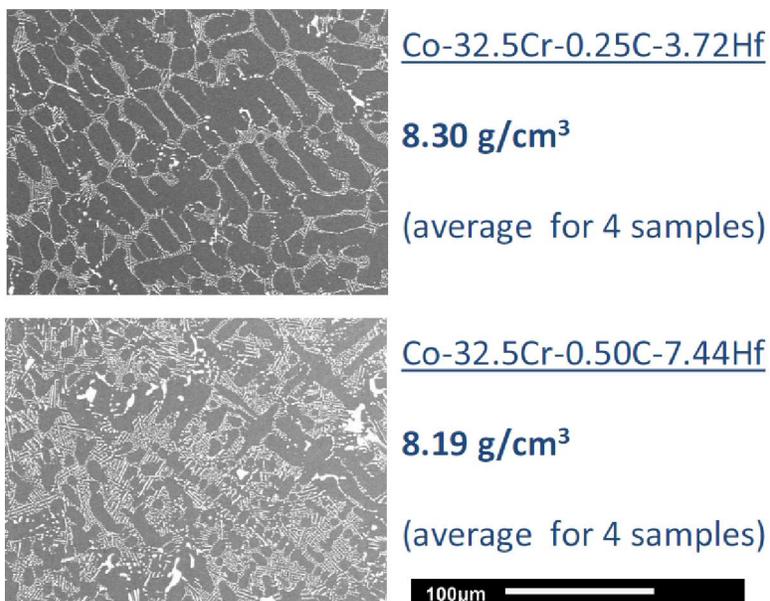
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Figure 5 : As-cast microstructures (SEM/BEC micrographs) and average densities of two Cr-enriched HfC-containing quaternary Co-25Cr-xC-yHf alloys

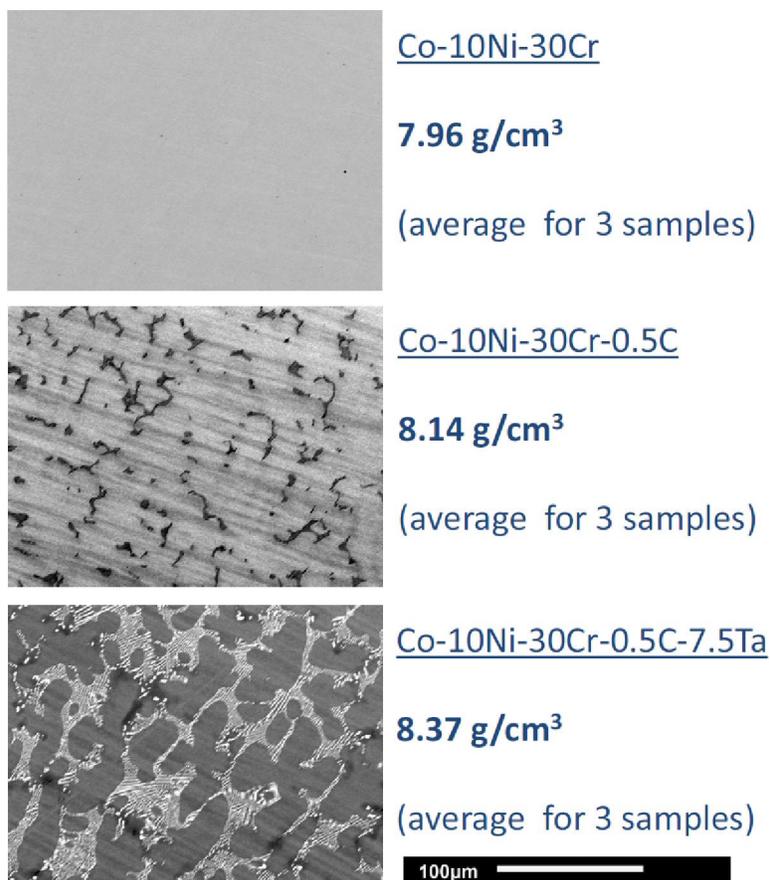


Figure 6 : As-cast microstructures (SEM/BEC micrographs) and average densities of three carbides-less or carbides-containing alloys based on Co-10Ni-30Cr

three alloys are respectively of about 8.1, 8.5 and 8.5 again.

The two alloys, the microstructures of which are

displayed in Figure 5, are chromium-enriched versions of the first and third alloys presented just above, since they contain 32.5 wt.% Cr instead only 25wt.%,

for the same C and Hf contents. This enrichment in chromium seems having had consequences on the as-cast microstructures of these alloys since the HfC interdendritic eutectic network of the first alloy is obviously denser than the one of the initial alloy, while it seems being the contrary for the second alloy. The volume mass of the first 32.5Cr alloy is now of about  $8.3 \text{ g/cm}^3$  and the one of the second Cr-enriched alloy is of about  $8.2 \text{ g/cm}^3$ .

The three last alloys are based on Co(bal.)-10Ni-30Cr, as many of the real cobalt-based superalloys for which the presence of 10wt.%Ni stabilizes the austenitic FCC crystallographic network of the cobalt-based matrix and 30wt.%Cr brings a really chromia-forming behaviour for the high temperature corrosion resistance. The first alloy seems single-phased (probably FCC solid cobalt with all the Ni and the Cr in solid solution) while chromium carbides (second alloy) and carbides mainly of the TaC type with the presence of some chromium carbides

(third alloy) are additionally present in the two other alloys (Figure 6). The density increases with the presence of carbides, especially when these ones are TaC carbides.

### Comparisons of the volume masses between alloys with chemical composition and microstructure considerations

As graphically shown in Figure 7 (chromium carbides) and in Figure 8 (tantalum carbides) the presence of  $\text{Cr}_x\text{C}_y$  carbides seems inducing a significant decrease in density while the inverse effect is obtained with tantalum carbides. The effect of the presence of HfC carbides seems intermediate to the previous ones since a significant decrease in volume mass seems resulting from the addition of almost 3.7wt.%Hf in a 0.25C-containing Co-25Cr alloy while no great effect is noted for an increase from 3.7 to

7.4wt.%Hf in a 0.50C-containing Co-25Cr al-

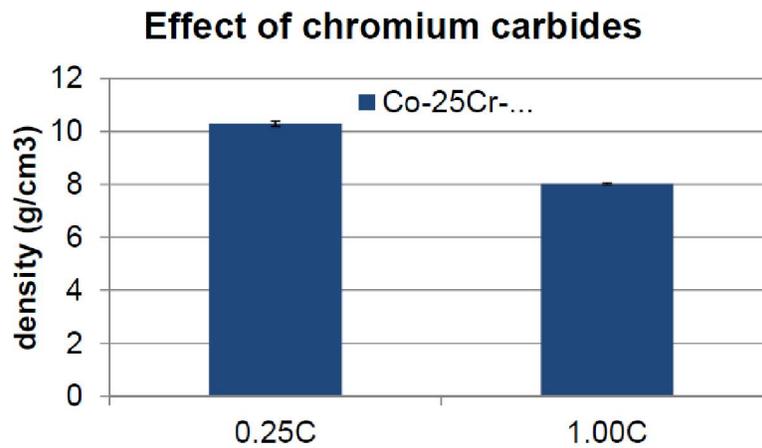


Figure 7 : Qualitative influence of the fraction in chromium carbides on the density of {Co-25Cr}-based alloys

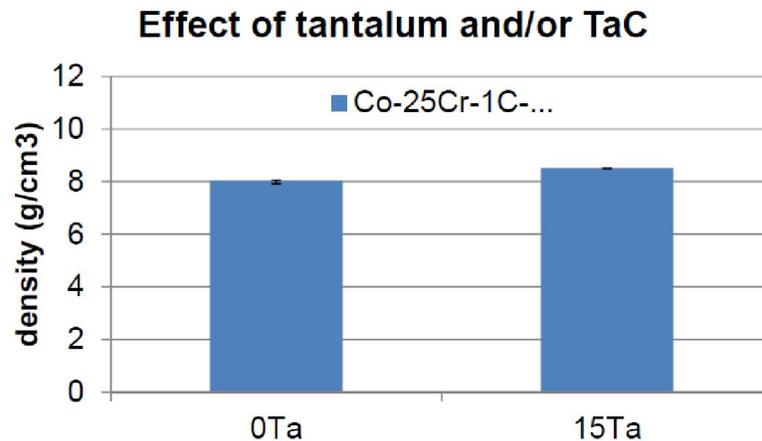


Figure 8 : Qualitative influence of the fraction in tantalum carbides on the density of {Co-25Cr-1C}-based alloys

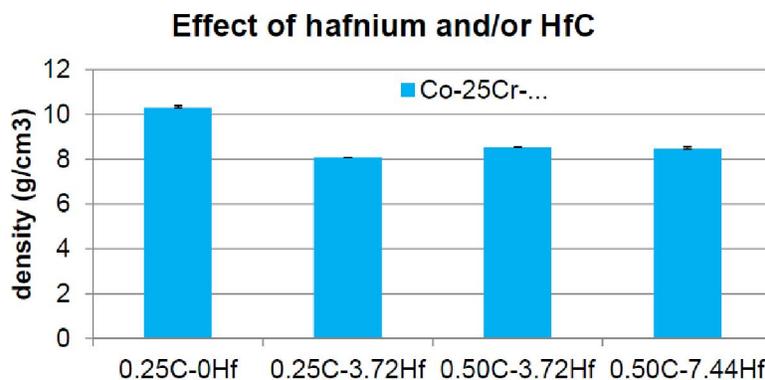


Figure 9 : Qualitative influence of the fraction in hafnium carbides on the density of {Co-25Cr}-based alloys

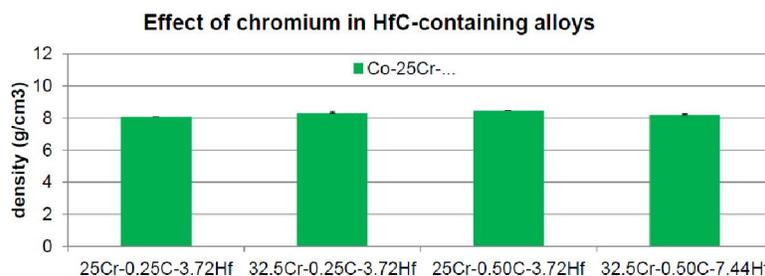


Figure 10 : Qualitative influence of the chromium weight content on the density of {Co-25Cr}-based alloys containing HfC carbides

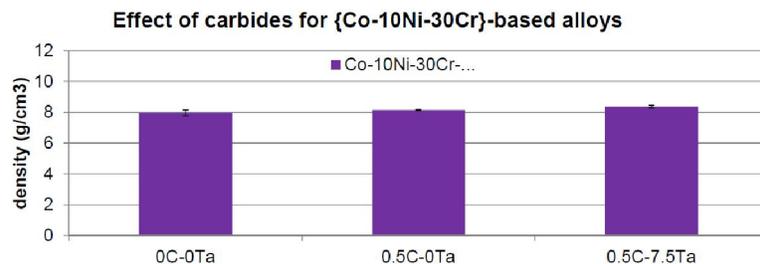


Figure 11 : Qualitative influence of the chromium weight content on the density of {Co-10Ni-30Cr}-based alloys without or with carbides

loy (Figure 9). Furthermore a chromium enrichment of such alloys did not change their volume mass (Figure 10). Concerning the Co-10Ni-30Cr alloys with or without carbides, the volume mass did not vary significantly with the presence or absence of carbides, whatever their nature (Figure 11).

### General commentaries

The elements present in the chemical compositions of all these cobalt-based alloys are Co, Ni, Cr, C, Ta and Hf, the room temperature densities (and structures) of which<sup>[16]</sup>, when they are pure and crystallized, are 8.9 (Co, complex hexagonal close packed), 8.9 (Ni, cubic close packed), 7.1 (Cr, body-centered cubic), 2.2 (C, graphite; 3.51 if diamond), 16.6 (Ta, body-centered cubic) 13.09 (Hf, close packed hexagonal). The densities of the carbides

sometimes met in the microstructures of these alloys are<sup>[17]</sup> 6.92 or 6.97 ( $\text{Cr}_7\text{C}_3$  or  $\text{Cr}_{23}\text{C}_6$ ) for the chromium carbides, 14.3 for the TaC carbides and between 11.8 and 12.6 for the HfC carbides.

Since the densities of the chromium carbides (7) are lower than the matrix one (about 8 for the carbide-free ternary Co-10Ni-30Cr alloy), the alloys containing chromium carbides ought to be less dense than a carbide-free alloy, which is not really the case for the Co-25Cr-1C while the alloy while the Co-25Cr-0.25C one is, on the contrary, denser (10.3). The first observation (which is the same for the Co-10Ni-30Cr 0 or 0.5C alloys) may be explained by the fact that, even for 1wt.%C, the formed carbides are not numerous and their fraction is low. The second one cannot be explained, at least easily, and con-

firmation is needed with future additional results. In contrast, the high density of the TaC carbides clearly induces an increase (+0.5) in density for a Co-25Cr base (but with rather high C and Ta contents: 1 wt.% and 15wt.% respectively) and, a little more limited (+0.4, due to only 0.5wt.%C and 7.5wt.%Ta, as is to say half the previous contents), for the Co-10Ni-30Cr base. The same tendency was seen for the HfC carbides (+0.4) for a Co-25Cr base. In the case of a Co-32.5Cr base two opposite results were obtained, and this is may be due to differences in HfC fractions due to the increase in chromium content (seemingly more HfC in the Co-25Cr-0.25C-3.72Hf alloy than in the 25Cr-containing initial version).

### CONCLUSIONS

Thus, except the curiously high volume mass obtained with the Co-25Cr-0.25C alloy, the densities of the studied alloys remained close to 8-8.5 g/cm<sup>3</sup>. This may have limited influence (less than +10% for the highest densities by comparison with the lowest ones) on the mass of the concerned component as well as on the values of the centrifugal stresses to which they may be submitted. But, in rare critical contexts, this may become important. Future work will focus of the understanding of these values, notably for the one of Co-25Cr-0.25C alloy, for example by performing X-ray diffraction to better specify the real single or double crystalline network of these as-cast samples which are not necessarily at thermodynamic equilibrium because the fast solidification and the high solid state cooling rate they knew. The presence of elements such as Ta and Hf in solid solution and the consequences on the density of the matrix also remains to be investigated.

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