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

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ABSTRACT

The density, a physical property of the alloys that is generally desired as low as possible when they are used in transportation (weight) or high speed centrifugal applications (mechanical stress), was measured in the case of several chromium-rich nickel-based and cobalt-based alloys containing different types of carbides. The results, simply obtained by the division of the mass by the volume both accurately measured on special samples, were given as average and standard deviation values. They confirmed for various microstructures that the {FCC matrix}-composed nickel-based alloys are denser that the {BCC matrix}-composed iron-based alloys. They additionally show that the presence of quantities of heavy elements Hf and Ta, and/or consequently of the corresponding dense MC carbides, leads to increases in density of almost +10% in some cases. This is to taken into account in the choice of such metallurgical mean for alloy structural strengthening, in addition to the increased in cost.

KEYWORDS

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

INTRODUCTION

Although met now much less frequently than γ/γ'-type superalloys, the chromium-rich nickel-based alloys still represent an important high temperature alloys' family. In some cases, some of them are used in the aero-engines and hot industrial processes[1,2] (resistance against hot corrosion favoured by several tens percents of chromium) as well as in low or room temperatures applications as prosthetic dentistry[3,4] in which high mechanical properties and resistance against aqueous corrosion are required (here too insured by chromium). Cr being a carbide-forming element the addition of carbon may lead to the development of carbides in such alloys, and with sufficient amounts of C and Cr together it is possible to promote at solidification hard particles useful for the wear resistance[5-8].

The alloys based on iron and containing also carbon also present a rather high hardness, which can vary over a rather wide range because of the presence of hard phases or compounds obtained by fast solidification[9] (cementite) or by quenching in solid state from the austenitic temperature range[10] (pearlite, bainite, martensite). In presence of Cr chromium carbides may be obtained to enhance the hardness of bulk iron-based materials[11] as well as coatings[12], but also possibly to reach high levels of mechanical resistance at high temperature.

In both cases, Ni-based and Fe-based, other carbides may be also obtained in the alloys, to particularly improve the mechanical properties at high temperature: Nb, Ta, Ti, Hf, Zr… Such elements may form MC carbides at different moments of solidification and with different shapes (blocky, script-like…). Since these elements are present in the bottom part of the Mendeleiev's periodic table their molar masses are greater than the ones of Ni, Fe and Cr and, furthermore, the carbides they form may have particularly high volume masses. This may have influence on the density of the whole alloys and thus inconvenience of their use: fuel overconsumption in transportation, enhancement of the centrifugal stresses… Thus it may be important to know the possible consequence of the choice of metallurgical means for the mechanical strengthening of the alloys, on the densities of the latter ones.

After the first one devoted to the cast cobalt-based family[13], this second study examines the case of several nickel-based alloys and iron-based alloys earlier studied for other properties. Here too one used several geometrically well-defined samples, issued from the same ingots as other metallographic or thermogravimetry samples previously tested and/or characterized: {chromium carbides} -containing alloys based on Ni[14] or Fe[15], {tantalum carbides}-rich alloys based on Ni[16] or Fe[17] and {hafnium carbides} – containing alloys based on Ni[14, 18, 19] or Fe[15, 20, 21]. Their densities were here too deduced from the volumes and masses of these samples, and the obtained results commented by regards to the chemical compositions and the microstructures.

EXPERIMENTAL

As for the cobalt-based alloys studied in the previous work[13], all the alloys considered here were earlier elaborated by foundry, from pure elements (Alfa Aesar, purity > 99.9wt.%) weighed to obtain the desired chemical compositions for an ingot of about 40g. The elaboration procedure was identical to the one followed for the cobalt alloys[13], as well as the metallographic preparation of the parallelepipeds. Their typical dimensions were 15mm-long (L), 2mm-width (l) and 1mm-thick (e). Their dimensions L, l and e were measured using an electronic calliper (precision 0.01mm). Their masses were measured using a precision balance (±0.1mg), allowing the determination of the volume mass $\rho = m / (L \times l \times e)$.

The samples destined to microstructure characterization were prepared as already described for the cobalt alloys[13]: embedding in cold resin mixture (resin CY230 + hardener HY256, ESCIL, France), grinding with SiC papers from 250–grit to 1200–grit, ultrasonic cleaning, polishing with textile disk enriched with 1µm-alumina particles, microstructure observations with a JEOL JSM 6010 LA Scanning Electron Microscope (SEM) in Back Scattered Electrons Composition mode (BEC).

RESULTS AND DISCUSSION

Nickel-based alloys

The first alloys subjected to the density determination are two ternary ones, Ni(bal.)-25Cr-0.50C and Co(bal.)-25Cr-1.00C (contents in weight percent). Both of them present a dendritic nickel 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) logically in greater quantity in the second alloy than in the first one (Figure 1). The average volume masses, respectively of about 8.2 and 7.9 g/cm^3, suggest that the carbide-richer alloy is a little 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 ratio rated to 1 led to TaC exclusively (white particles), with a particularly high volume fraction (Figure 2). The obtained volume mass, about 8.6 g/cm^3,

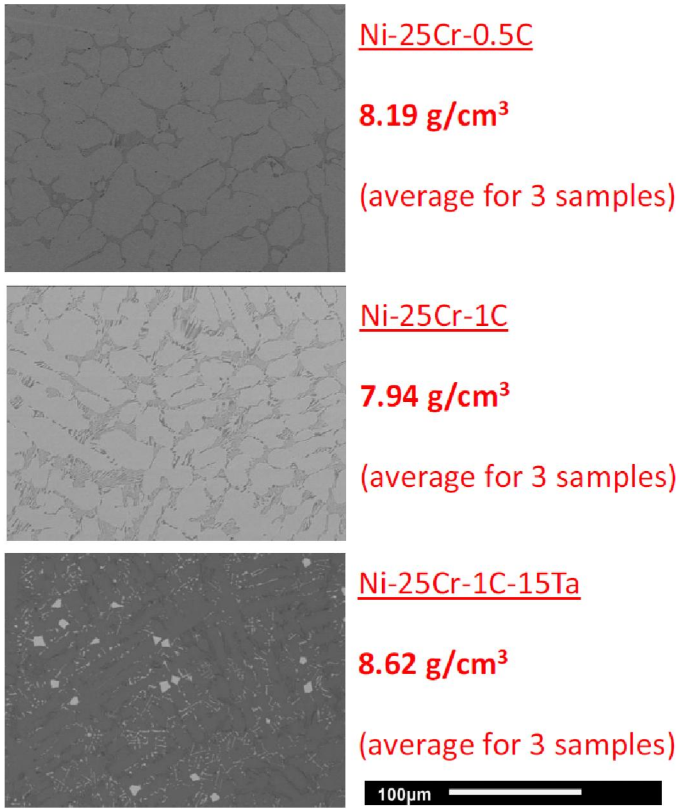

Figure 1 : As-cast microstructures (SEM/BEC micrographs) and average densities of the two ternary Ni-25Cr-xC alloys and of the TaC-rich quaternary Ni alloy

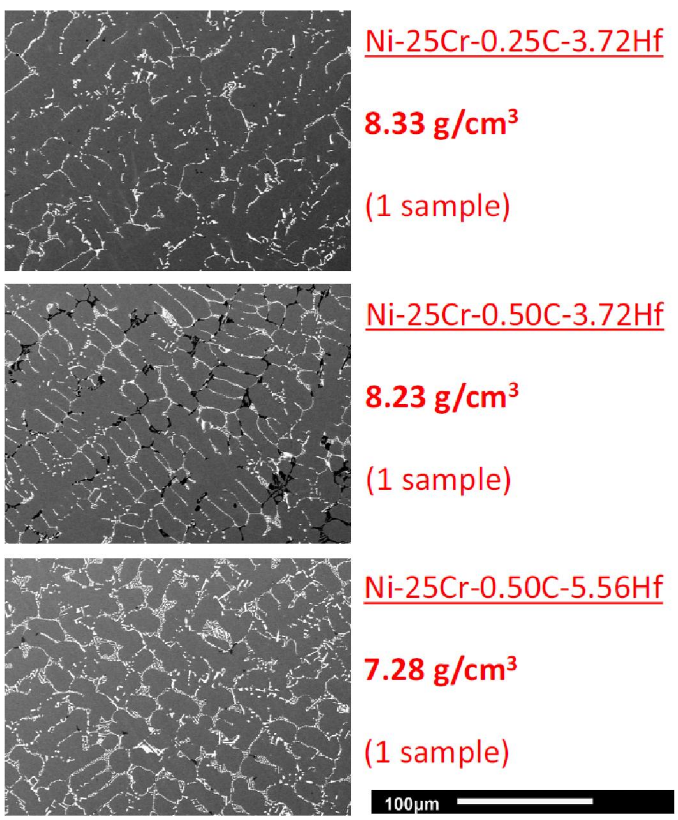

Figure 2 : As-cast microstructures (SEM/BEC micrographs) and average densities of several HfC-containing quaternary Ni-25Cr-xC-yHf alloys

is significantly higher than 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 2). These hafnium carbides (white particles) are essentially eutectic ones only (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-5.56Hf alloy. This is thanks to the Hf/C atomic ratio of 1 or not far from 1, that the first and third alloys only contain HfC and no chromium carbide is present. The densities of these three alloys are respectively of about 8.3, 8.2 and 7.3.

Iron-based alloys

The first Fe-based alloy which was subjected to the density determination is a ternary Fe(bal.)-25Cr-1.00Cone (contents in weight percent). It presents a dendritic iron matrix of solid solution in which some of the chromium and carbon atoms are dissolved (Figure 3), as well as interdendritic chromium carbides (grey particles darker than matrix, either Cr_7C_3 or $Cr_{23}C_6$). Its average volume mass is of about 7.4 g/cm^3. The second alloy is a quaternary one based on Fe-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 ratio rated to 1 led to TaC exclusively (white particles), with a particularly high volume fraction. The obtained volume mass, about 7.7 g/cm^3, is significantly higher than for previous Ta-free corresponding alloy.

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 (angular blocky compact) and eutectic ones only (script-like, mixed with matrix in the interdendritic spaces). Chromium carbides (darker than matrix) are present too in the 0.50C-3.72Hf and 0.50C-5.56Hf alloys for which the Hf/C atomic ratio is lower than 1. The densities of these three alloys are respectively of about 7.6, 7.6 and 7.5, as is to say almost the same.

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

As graphically shown in Figure 5 (chromium carbides in Ni-based ternary alloys) and in Figure 6 (tantalum carbides in Ni-based and Fe-based alloys) the presence of more Cr_xC_y carbides seems inducing a slight decrease in density while the inverse

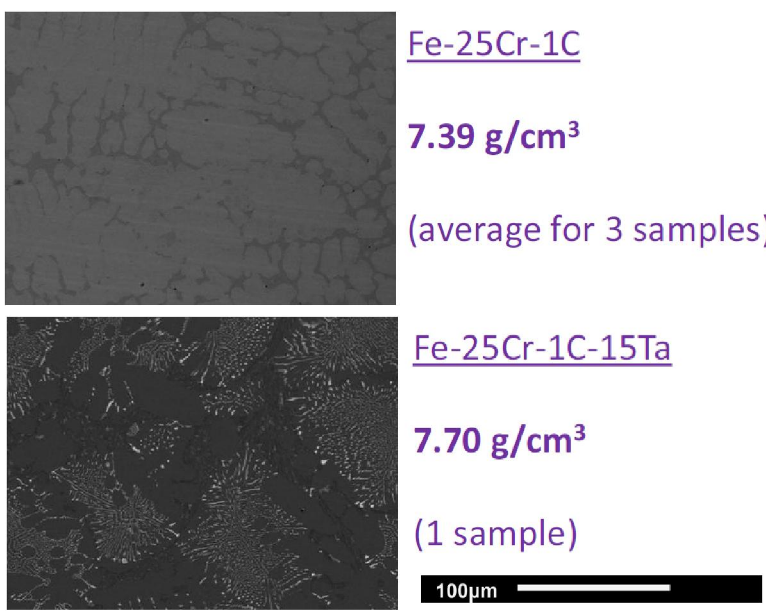

Figure 3 : As-cast microstructures (SEM/BEC micrographs) and average densities of a ternary Fe-25Cr-1C alloy and of its corresponding TaC-rich quaternary Fe alloy

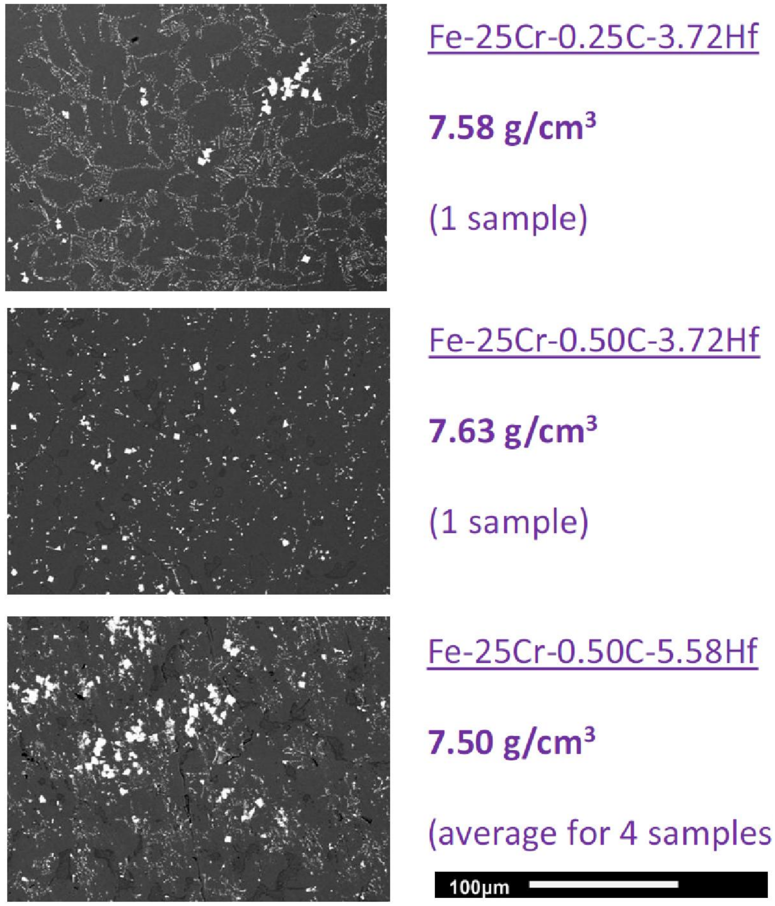

Figure 4 : As-cast microstructures (SEM/BEC micrographs) and average densities of several HfC-containing quaternary Fe-25Cr-xC-yHf alloys

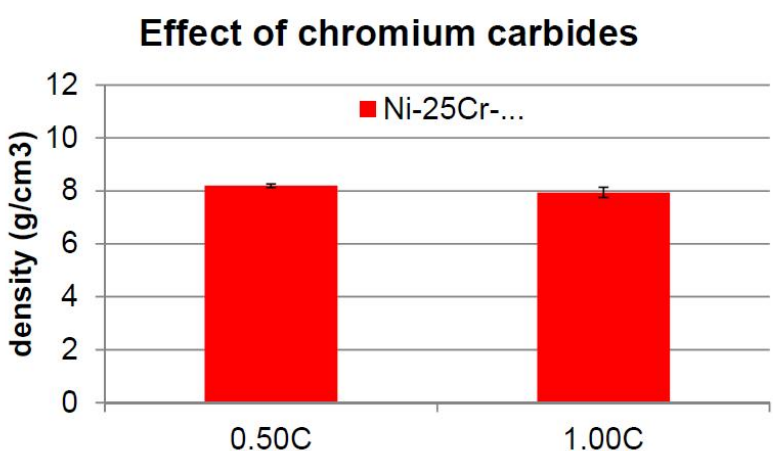

Figure 5 : Qualitative influence of the fraction in chromium carbides on the density of {Ni-25Cr}-based alloys

effect is obtained with tantalum carbides. The effect of the HfC carbides (Figure 7) is not really clear since the density variations between the alloys of a same family are very little. However it seems that the density tends very slightly decreasing when the carbon content and/or the Hf content increase, as is to say when the HfC fraction increases, for the Ni-based alloys as well as for the iron-based ones.

General commentaries

The elements present in the chemical compositions of all these nickel-based and iron-based alloys are Ni, Fe, Cr, C, Ta and Hf, the room temperature densities (and structures) of which[22], when they

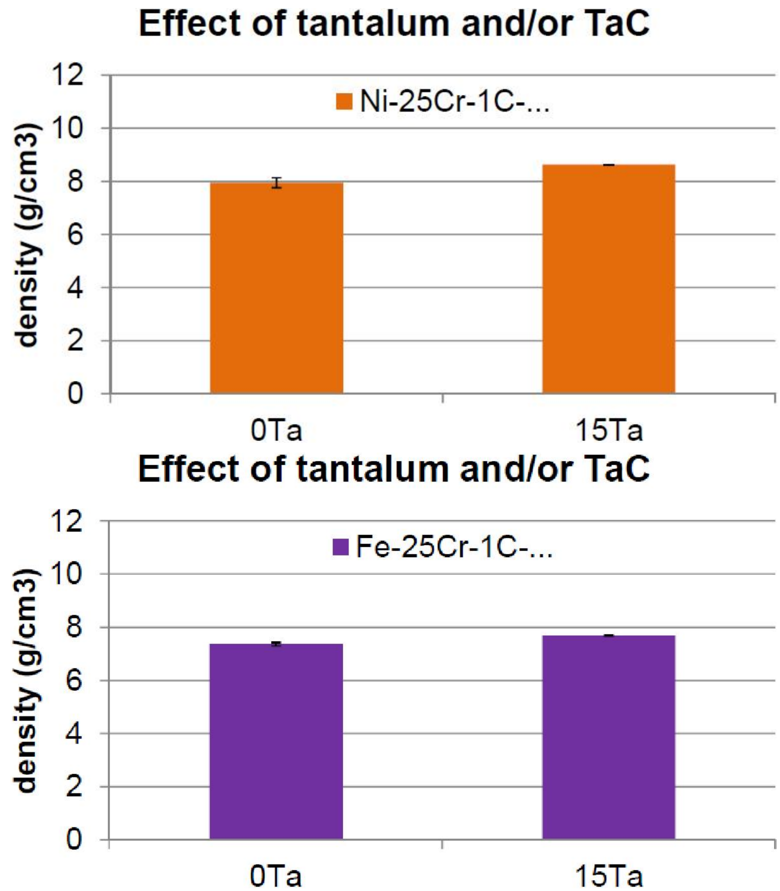

Figure 6 : Qualitative influence of the fraction in tantalum carbides on the density of {Ni-25Cr-1C}-based and {Fe-25Cr-1C}-based alloys

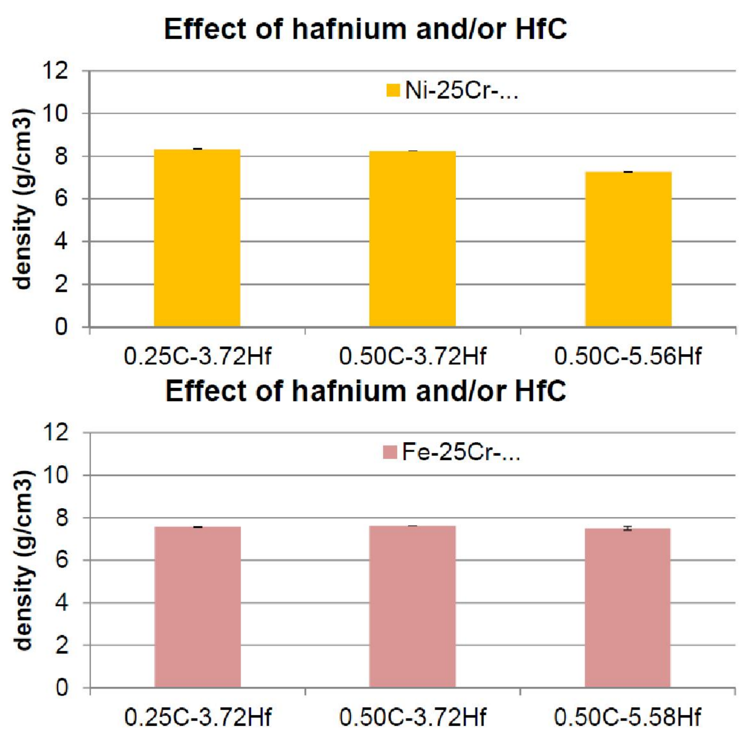

Figure 7 : Qualitative influence of the fraction in hafnium carbides on the density of {Ni-25Cr}-based alloys and {Fe-25Cr}-based alloys

are pure and crystallized, 8.9 (Ni, cubic close packed), 7.86 (Fe, body-centered cubic), 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[23] 6.92 or 6.97 (Cr_7C_3 or $Cr_{23}C_6$) 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 Ni-25Cr0.5C alloy in which the carbides do not represent a significant fraction), the alloys containing more chromium carbides ought to be less dense than a carbide-free alloy, which is here the case of the Ni-25Cr-1C. The high density of the TaC carbides clearly induces an increase (+0.7 if M=Ni and +0.3 if M=Fe) in density for a M-25Cr base for rather high C and Ta contents: 1wt.% and 15wt.% respectively. In contrast this was not really observed for the HfC carbides for which this was maybe more the inverse effect. It is true that chromium carbides were also present in some cases and brought a negative contribution.

CONCLUSIONS

Thus, the volume masses of all the Ni-based alloys studied here remained close to $8 g/cm^3$ for the {Hf,Ta}-free alloys, very close to the Co-25Cr-1C alloy of the previous study[13]. The addition of 4 to 6 wt.% Hf, and especially of 15 wt.% Ta, induced a significant increase in density (up to 8.6), comparable to what was observed for the corresponding cobalt alloys[13]. The FCC (and probably also partly HCP for the as-cast Co-alloys[13]) compact crystalline network of the present nickel-based alloys and the former cobalt-based alloys led for them to higher densities that the ones (7.4-7.7) of all the present iron-based alloys the matrixes of which are mainly BCC as is to say not so compact. However the introduction of Hf or Ta in the latter ones has as consequence an increase in density which comes rather close to 8. To summarize, this is more the matrix and its crystalline network that is important for the global density of the alloys than the carbides even formed with heavy elements such as Ta or Hf. Effectively this goes on separating the densities into two parts, one lower than 7.8 and one higher than 8. However the presence of a quantity of carbides great enough may significantly influence the density: limited decrease if chromium carbides, more important increase if MC carbides when M is a heavy metallic element (e.g. Hf or Ta instead Ti and V for example, and even Nb).

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