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Thermal expansion of cobalt-based, nickel-based and iron-based cast alloys reinforced by chromium carbides

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ABSTRACT

Six 30wt.%Cr-containing alloys reinforced by chromium carbides, two ones based on cobalt, two ones based on nickel and two other ones based on iron, were elaborated by foundry way and studied in thermal expansion between 100°C and 1200°C, for two microstructure orientations favoured by special cutting. The heating parts, isothermal parts and cooling parts were quantitatively analysed. The main global differences of thermal expansion were obtained between the alloys based on Co or Ni (high expansion) and the ferritic Fe-based alloys (low expansion). A higher amount of carbon or carbides generally led to slower dilatations and to enhance attenuation of expansion due to crystallographic changes of matrix. This also leads to a compressive deformation of matrix at the highest temperatures, due to the differential expansion between the two phases from room temperature and these high temperatures. Negative permanent deformations were thus obtained for the alloys. © 2010 Trade Science Inc. - INDIA

KEYWORDS

INTRODUCTION

Increasing the temperature usually induces a dimensional expansion for the metallic alloys, with consequently the possible appearance of internal stresses when they are not free to deform or when the whole considered piece is not homogenous in temperature. This is particularly true for refractory alloys when their average temperature varies between room temperature and more than 1000°C[1]. To reduce such stresses, one usually looks for lowering the thermal expansion coefficient. Among the possible parameters able to influence the thermal expansion there are the chemical composition of the alloy and the local microstructure orientation of the cast alloys.

The purpose of this study is to analyse the possible effects of these parameters on the thermal expansion behaviour of selected metallic alloys which are especially refractory and which can be considered as the bases of most of the superalloys used at high temperatures in corrosive atmospheres.

EXPERIMENTAL

Two cobalt-based alloys, two nickel-based alloys and two iron-based alloys, all containing 30 wt.%Cr and either 0.2 wt.%C or 0.4 wt.%C, were elaborated by High Frequency induction foundry from pure ele-

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ments (each ingot being of about 100g). Their chemical compositions were verified by EDS* measurements with the apparatus equipping a SEM** (*: Energy Dispersion Spectrometry, **: Scanning Electron Micro-
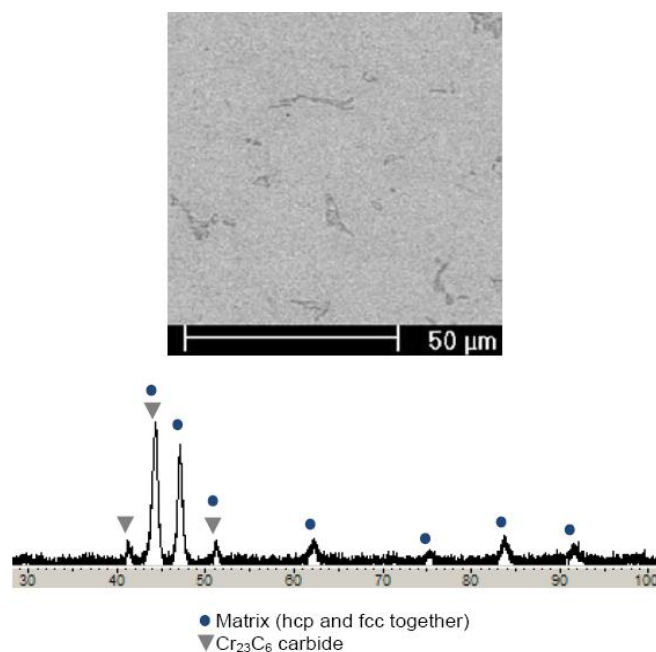

Figure 1 : Microstructure of the Co-30Cr-0.4C alloy (Scanning electron microscope, Back scattered electrons mode) and X-Ray diffraction spectrum revealing the {hcp+fcc}-matrix and the $Cr_{23}C_6$ carbides
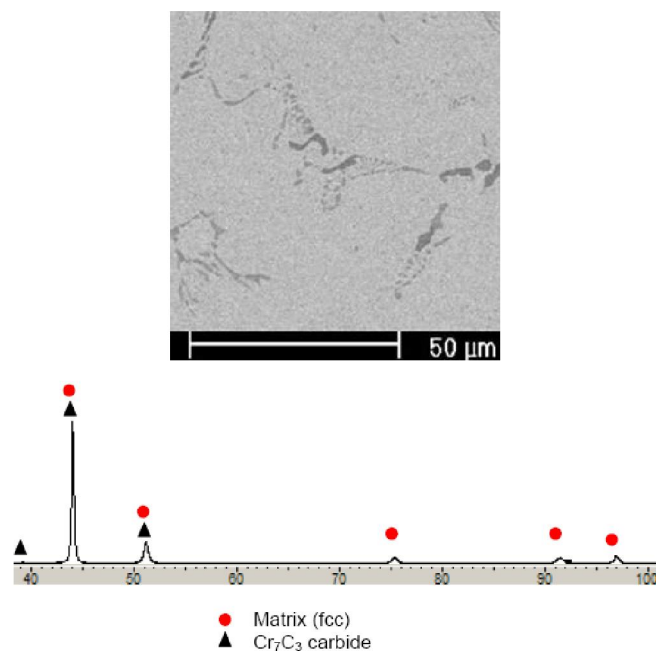

Figure 2 : Microstructure of the Ni-30Cr-0.4C alloy (Scanning electron microscope, Back scattered electrons mode) and X-Ray diffraction spectrum revealing the fcc-matrix and the Cr_7C_3 carbides
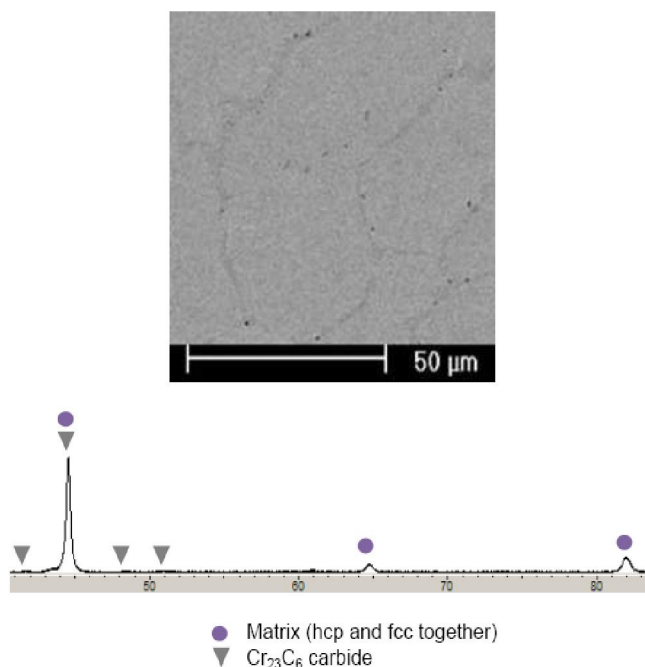

Figure 3 : Microstructure of the Fe-30Cr-0.4C alloy (Scanning electron microscope, Back scattered electrons mode) and X-Ray diffraction spectrum revealing the bcc-matrix and the $Cr_{23}C_6$ carbides

scope), while figure 1 (cobalt alloys), figure 2 (nickel alloys) and figure 3 (iron alloys) illustrate the microstructures of the obtained alloys (SEM Philips XL30, Back Scattered Electrons mode, accelerating voltage of 20kV) with control by X-Ray Diffraction (XPERT Pro, 1.54 A). There are composed:

- of a matrix based on the main element of the alloy (Co: hcp or fcc, Ni: fcc and Fe: bcc) and containing the most part of chromium, as well as a part of carbon, in solid solution;

- chromium carbides in the interdendritic spaces, Cr_7C_3 (Ni-based alloys) or $Cr_{23}C_6$ (Fe-based alloys and Co-based alloys) with logically a fraction in the 0.4C-containing alloy higher than in the 0.2C-containing one.

The parallelepiped samples, the dimensions of which were about 4mm $\times$ 4mm $\times$ 2.5mm* (*: thickness along which dilatation was measured), were cut either for characterizing thermal expansion in the average direction of dendrites (i.e. parallel to the thermal gradient existing during solidification[2], "Orientation 1"), or perpendicularly to dendrites (i.e. in the direction perpendicular to this thermal gradient, "Orientation 2"), as described in figure 4. The thermal expansion was characterized using a Setaram TMA 92-16.18 thermo-

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dilatometer:
- during the heating from room temperature up to 1200°C (heating rate: 10 °C / min),
- during the 600 seconds-isothermal dwell at 1200°C
- and during the cooling down to room temperature (cooling rate: -20 °C / min).

The curves were cut in order to remove the parts bellow 100°C affected by perturbations due to a thermal equilibrium not yet achieved. Only the parts above 100°C were thus considered for characterization.
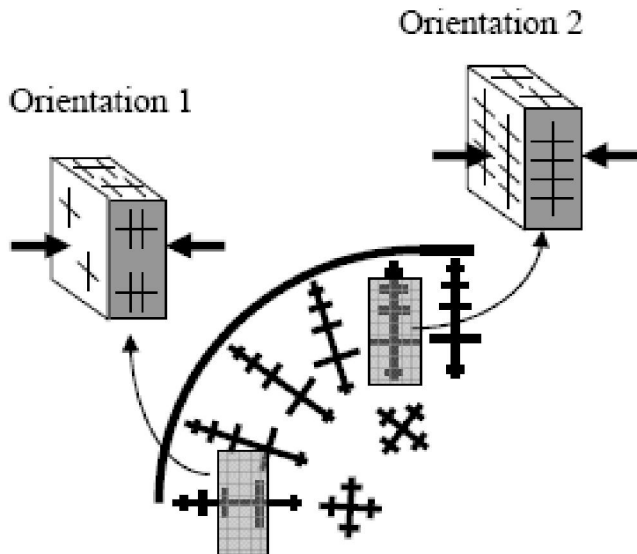

Figure 4 : Scheme describing how the two samples per alloy were cut in an ingot for characterizing the eventual anisotropy of thermal expansion

RESULTS AND DISCUSSION

General aspect of the dilatometry curves

The obtained dilatometry curves are presented in figure 5 for the two cobalt alloys, in figure 6 for the two nickel alloys and in figure 7 for the two iron alloys, with in the same graph the dilatometry curves for the two orientations together.

One can first remark that the dilatometry curves (their heating part or cooling part) are generally continuous. Nevertheless there are two cases (Co-30Cr-0.2C alloy for the two orientations) for which there are small jumps in the curves near 960°C (heating parts) and 840°C/1000°C (cooling parts, depending on the orientation). There are related to the hcp → fcc (heating) and fcc → hcp (cooling) allotropic change of matrix which occurs at these levels of temperature, like

for a binary Co-30Cr alloy[3]. However, such jumps are not visible on the dilatometry curves of the Co-30Cr-0.4C alloy, despite that the same crystallographic transformation must theoretically act too in this second alloy[4], for a temperature slightly lower than for Co-30Cr-0.2C. This inhibition, by the interdendritic
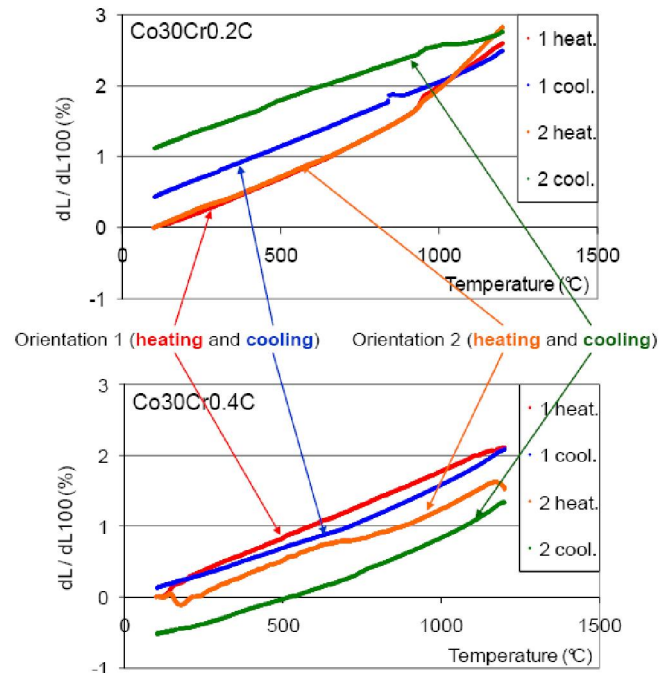

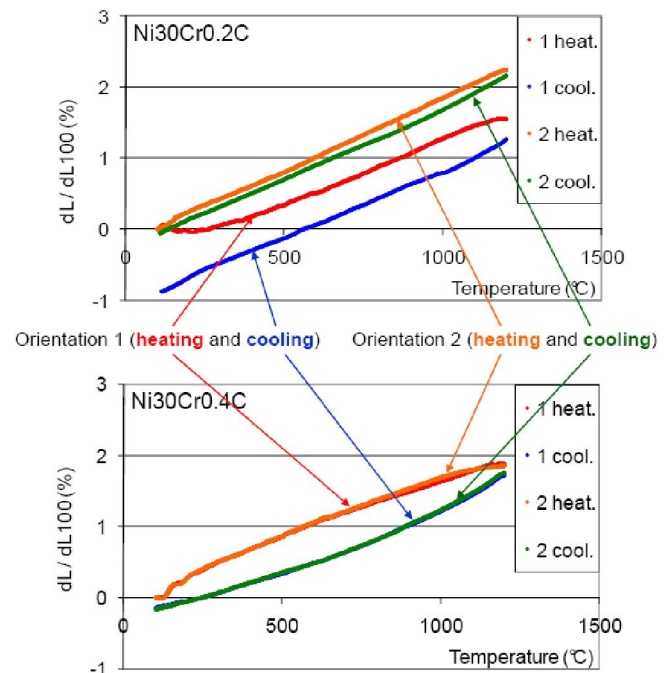**Figure 5 : Thermal expansion of the two cobalt alloys for the two orientations**

Figure 6 : Thermal expansion of the two nickel alloys for the two orientations
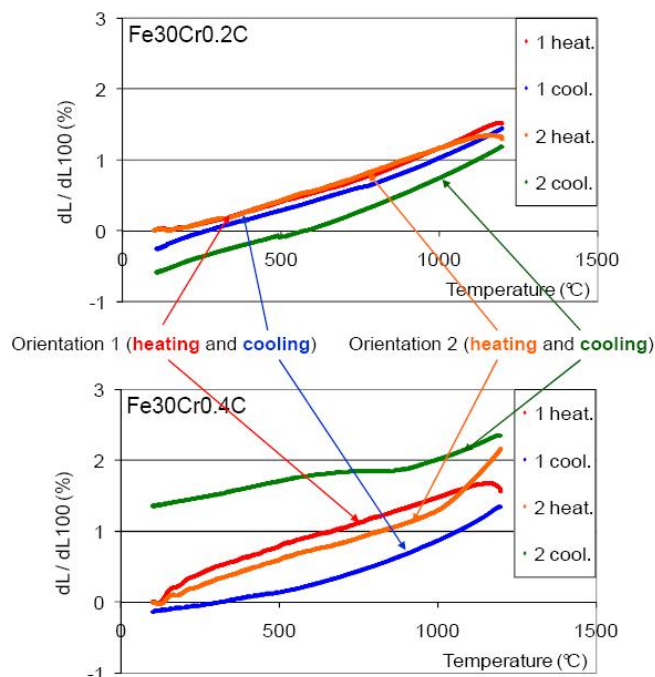
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Figure 7 : Thermal expansion of the two iron alloys for the two orientations

carbides, of the expansion due to the hcp $\leftrightarrow$ fcc matrix changes, which can be encountered with a Co-30Cr-0.8C alloy[3], obviously exists also for 0.4wt.%C. Such phenomenon does not occur neither in the nickel alloys, the matrix of which remains fcc on the whole temperature range[5,6], nor in the iron alloys the matrix of which is always bcc[5,7].

A second observation which can be done is a deceleration which acts in most cases before reaching the maximal temperature, except only the Co-30Cr-0.2C alloy for the two orientations and the Fe-30Cr-0.4C alloy for the orientation 2 for which there is a curious phenomenon of rapid increase in thickness. This deceleration of expansion, which can be sometimes followed by a contraction at the very end of heating (e.g. Co-30Cr-0.4C orientation 2 or Fe-30Cr-0.4C orientation 1), is often followed by an isothermal progressive contraction during the dwell at 1200°C.

Thirdly, it appears that the heating part and the cooling part are almost never exactly superposed (except Ni-30Cr-0.4C for the two orientations). The heating part and the cooling part are also close to one another in the case of Ni-30Cr-0.2C (orientation 2) and Co-30Cr0.4C (orientation 1), while they are clearly distinct in all the other cases. Furthermore, except two curious cases (Co-30Cr-0.2C two orientations and Fe-

30Cr-0.4C orientation 2 only), the cooling part tends to be situated under the heating part, more or less.

Quantitative analysis of the curves

To further observe the dilatometry measurements, one can exploit the curves in order to obtain the total deformations at heating and at cooling between 100°C and 1200°C, as well as the isothermal deformation (TABLE 1). One can see that the deformation at heating seems generally higher than the contraction at cooling for the cobalt alloys, while there is no real difference for the nickel alloy (deformations at heating and at cooling almost equal). For the iron alloys, differences exist but without systematic hierarchy between heating and

TABLE 1 : Deformations during the temperature-increasing part of the curves, the isothermal dwell and the temperature-decreasing part

Alloy		$\dfrac{\Delta\varepsilon_{100 \to 1200}\,(\%)}{\Delta\varepsilon_{1200 \to 1000}\,(\%)}$	$\Delta\varepsilon_{T=1200}$ (%)
	Orientation 1		
	Orientation 2	$\dfrac{\Delta\varepsilon_{100 \to 1200}\,(\%)}{\Delta\varepsilon_{1200 \to 1000}\,(\%)}$	$\Delta\varepsilon_{T=1200}$ (%)
Co-30Cr-0.2C	Orientation 1	2.597 / -2.063	-0.104
	Orientation 2	2.827 / -1.641	-0.068
Co-30Cr-0.4C	Orientation 1	2.118 / -1.948	-0.040
	Orientation 2	1.517 / -1.865	-0.178
Ni-30Cr-0.2C	Orientation 1	1.542 / -2.136	-0.283
	Orientation 2	2.233 / -2.214	-0.080
Ni-30Cr-0.4C	Orientation 1	1.861 / -1.859	-0.144
	Orientation 2	1.845 / -1.914	-0.095
Fe-30Cr-0.2C	Orientation 1	1.515 / -1.701	-0.071
	Orientation 2	1.293 / -1.780	-0.100
Fe-30Cr-0.4C	Orientation 1	1.563 / -1.482	-0.213
	Orientation 2*	2.161 / -0.997	+0.192

(*: unusual curve for the cooling part)

cooling. That is also true concerning the orientations. The Co-30Cr-0.2C alloy displays a thermal expansion more pronounced than the Co-30Cr-0.4C one while no such difference seems to exist for the nickel alloys and the iron alloys. On the contrary there are significant differences about the thermal expansions or contractions over the 100-1200°C range between the three alloys families: they are higher for the cobalt alloys than for the nickel alloys and higher for the two later ones than for the iron alloys.

The preceding differences about deformation between 100 and 1200°C can be found again with the average coefficients of thermal expansion over the 250-750°C ranges (TABLE 2) for which the curves are locally almost linear. The thermal expansion coefficients

TABLE 2 : Average values of the corresponding thermal expansion coefficients and of the isothermal deformation rates

Alloy		av. $\alpha_{250 \to 750}$ $(\times10^{-6}$°$C^{-1})$ / av. $\alpha_{750 \to 250}$ $(\times10^{-6}$°$C^{-1})$	average $\Delta\varepsilon/\Delta t$ at 1200°C (% / s)
Co-30Cr-0.2C	Orientation 1	19.68 / 18.04	- 0.173 × 10⁻³ % / s
	Orientation 2	18.62 / 15.90	- 0.113 × 10⁻³ % / s
Co-30Cr-0.4C	Orientation 1	18.50 / 14.98	- 0.067 × 10⁻³ % / s
	Orientation 2	15.76 / 14.78	- 0.297 × 10⁻³ % / s
Ni-30Cr-0.2C	Orientation 1	15.78 / 17.98	- 0.472 × 10⁻³ % / s
	Orientation 2	19.64 / 19.02	- 0.133 × 10⁻³ % / s
Ni-30Cr-0.4C	Orientation 1	17.64 / 14.40	- 0.240 × 10⁻³ % / s
	Orientation 2	17.72 / 14.52	- 0.158 × 10⁻³ % / s
Fe-30Cr-0.2C	Orientation 1	12.56 / 12.64	- 0.118 × 10⁻³ % / s
	Orientation 2	13.28 / 12.76	- 0.167 × 10⁻³ % / s
Fe-30Cr-0.4C	Orientation 1	14.38 / 9.62	- 0.355 × 10⁻³ % / s
	Orientation 2*	13.56 / 7.38	+ 0.320 × 10⁻³ % / s

(*: unusual curve for the cooling part)

are slightly higher for the cobalt alloys than for the nickel alloys, but the later ones are significantly higher than for the iron alloys. One can also say that the thermal expansion coefficients tend to be higher for the heating than for the cooling for all the alloys. However the orientation has an importance essentially for the cobalt alloys for which the orientation 1 led to higher coefficients than for the orientation 2. Concerning the average deformation rates during the 1200°C-isothermal stage the same comments as for the total deformation at 1200°C can be logically done.

General commentaries

Several differences have been found for the thermal expansion and contraction behaviours of these six alloys. The main one is between on the one hand the cobalt alloys (hcp/fcc then fcc matrix) and nickel alloys (fcc matrix) the thermal expansion of which is strong (average coefficient of about $17\text{-}20 \times 10^{-6}$ °C^{-1}), and on the other hand the iron alloys the matrixes of which are bcc over the whole studied temperature range ($12\text{-}14 \times 10^{-6}$ °C^{-1}). Such differences are classical between an austenitic alloy and a ferritic one, like in the well-known case of pure iron (bcc and slow thermal expansion between room temperature and about 910°C then fcc and faster thermal expansion up to temperature higher than 1200°C).

The carbon content has also an effect on the average coefficient of thermal expansion, but only for the cobalt alloys and the nickel alloys for which the matrixes tend to display thermal expansion significantly faster than for the carbides (about 10×10^{-6} °C^{-1} for the Cr_7C_3 as well as for the $Cr_{23}C_6$ carbides[8]). On the contrary, for the iron alloys the thermal expansion of which is slower and consequently closer to the carbides ones, the volume fraction of carbides and the carbon content have less importance.

Concerning the microstructure orientation, results showed that this parameter can influence the thermal expansion. This was observed here more for the cobalt alloys than for the two other alloy families, with average coefficients higher for a dilatation parallel to dendrites than for the perpendicular orientation (between 250 and 750°C). The same order was previously reported[3] for M-30Cr-O.8C alloys. Even for the alloys studied here and which contain less carbon, the carbides seem

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imposing their low dilatation and then reducing the thermal expansion in the direction along which the dendrites are not continuous but juxtaposed.

The more visible effect of carbides appeared at the end of heating, when temperature has become high enough to sufficiently weaken the metallic matrix for permitting its compressive deformation by the carbides releasing their tensile-stressed state due to the difference of thermal expansion between these two phases[3]. This was already observed for M-30Cr-0.8C alloys (M=Ni, Co or Fe), and also for ternary alloys richer in carbon[9].

Another effect of carbides is the attenuation (Co-30Cr-0.2C) or inhibition (Co-30Cr-0.4C) of the jump due to the hcp $\rightarrow$ fcc transformation of the matrix occurring near 900°C, as earlier observed for a Co-30Cr-0.8C alloy by comparison with a binary Co-30Cr alloy[3]. This leads to think that there is a critical chromium content, situated between 0.2C and 0.4C, bellow which carbides are not able to smooth the expansion jump due to the hcp $\rightarrow$ fcc matrix change (jump due to the disorder caused by the rearrangement and not to a change of compactness which does not exist between these two crystals), and above which the jump is inhibited by the carbides network.

CONCLUSIONS

Thermal cycles applied to carbides-containing alloys often lead to not reversible expansion / contraction dimensional changes, with consequently residual negative deformation which can depend on the microstructure orientation and on the carbide fraction. This probably results in a volume contraction (and then a density slightly increased) with a matrix stressed in compression. This phenomenon can be related to the difference of thermal expansion coefficient between the metallic matrix and the carbide phase (ratio 2:1 for the cobalt or nickel matrixes, and 3:2 for the iron ferritic matrix). More than a clear dependence on the microstructure orientation one can more simply consider than the thermal expansion is often not isotropic, as concluded previously for such ternary alloys richer in carbon (up to 2wt.%)[9].

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