# *Materials Science*

# Study of the thermal expansion and the dimensional stability at high temperature of carbides-containing cobalt alloys

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## ABSTRACT

Two cobalt-based alloys, a ternary one (Co-30Cr-0.3C) and a quaternary one (Co-30Cr-0.3C-4.5Ta) were elaborated by foundry and their thermal expansion behaviour tested by dilatometry. Three cycles {heating from room temperature – two hours – stage at 1050, 11150, 1200 or 1250°C – cooling to room temperature} were applied to samples cut in the ingots. The thermal expansion of the ternary alloy (containing low fraction of chromium carbides) was almost linear and reproductive while curious phenomena occurred for the quaternary alloy (containing high fraction of tantalum carbides). During the high-temperature 2-hours stage of each cycle the samples continued to deform. The amounts of these isothermal deformations were studied versus the number of the considered cycle, versus temperature and versus the type of alloy. After examination of the changes involved by the thermal cycles on the microstructures of the alloys, it appears that the accumulation of stresses in the matrix and in the carbides during the heating because of their interaction due to their difference of thermal expansion coefficient was not the single cause. Indeed carbides have significantly evolved: decreased volume fractions of chromium carbides and fragmentation of tantalum carbides.
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## INTRODUCTION

An important family of metallic materials for high temperature oxidation are the cobalt-base superalloys. These alloys, available in cast or wrought versions[1], generally contain several tens of chromium to resist high temperature oxidation (e.g. by combustion gases[2]) and corrosion (e.g. by molten glass[3]), properties of chemical resistance at high temperature allowing their use as glass-forming tools[4]. These alloys display high mechanical properties up to rather high temperatures, thanks to the intrinsic strength of the austenitic matrix of the cobalt, its solid-solution hardening by presence of heavy atoms (e.g. W or Re), and/or their precipitation hardening by carbides (e.g. $(Cr,Co)_7C_3$ or TaC) appeared in interdendritic spaces at solidification (coarse eutectic carbides) or later during specific heat-treatments (fine dispersed carbides).

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Concerning specifically these latter cobalt-based superalloys, which finally consist in the association of a ductile continuous matrix and of reinforcing dispersed hard particles, as is to say as a kind of in situ composite material, the co-existence of such two very different phases may lead to internal phenomena in some situations. For example, the differences of thermal expansion behaviour between the high-dilatation metallic matrix and the low-dilatation ceramic carbide particles, may cause interactions at the microstructure scale, with possibly curious macroscopic behaviour for pieces made of such alloys, as previously evidenced and interpreted in the case of ternary or quaternary equiaxed Co-based, Ni-based and Fe-based alloys[5,6] for example. It was noticed that after heating to rather high temperatures, during which a mechanical equilibrium persists between a matrix more and more in compression and a carbides network more and more in traction, the high temperature – induced weakening of the matrix promotes a visco-plastic deformation of the now too softy matrix under the compression stresses applied by the carbide network. Such phenomenon can be observed during the isothermal stage at 1200°C separating heating and cooling, and in some cases, it can ne already revealed by the shape of the high temperature part of the heating dilatometry curve.

The purpose of this work is to deepen the knowledge of the dimensional consequences of this microstructure interaction for a model cobalt alloy and a little more complex one, by measuring their dimensional variation in isothermal conditions for different high temperatures.

## EXPERIMENTAL

### Choice and synthesis of the alloys

The two alloys which were considered for this study are a simple ternary Co-30Cr-0.3C alloy and a quaternary Co-30Cr-0.3C-4.5Ta alloy. Their elaborations were achieved using a high frequency induction furnace (CELES) under an inert atmosphere of 300mbars argon. The melting at a little more than 100kHz-4kV was realised on less than 4 minutes, the alloys were maintained in the molten state during three minutes to be sure to have entirely melted and/or dissolved (Ta) the pure metals and graphite of the mix,

and homogenized the obtained liquid, before starting the liquid state then solid state cooling. After complete cooling, the ingots (between 30 and 40g) were cut using a Isomet 5000 precision saw from Buehler, in order to obtain:

-   cold resin - embedded and mirror like - polished samples for metallographic observations (done using a JEOL J7600F Field Emission Gun - Scanning Electron Microscope in Back Scattered Electrons mode, acceleration voltage: 20kV),
-   and parallelepipeds (about 5 x 5mm² x 3mm (thickness, measured dilatation direction).

### Dilatometry runs

The dilatometry tests were performed using a TMA92-16.18 apparatus from Setaram. They consisted in cycles composed of:

-   a heating at 10°C min$^{-1}$ from room temperature to the targeted high temperature,
-   an isothermal stage of 2 hours at this temperature,
-   a cooling at -10°C min$^{-1}$ down to room temperature.

For an alloy and a given targeted stage high temperature, this cycle was repeated three times.

The stage temperatures were chosen to be 1050°C, 1150°C and 1200°C for the Co-30Cr-0.3C alloy while it was 1250°C for the Co-30Cr-0.3C-4.5Ta alloy.

### Initial thermodynamic calculations

In order to help if necessary for the interpretation of the dilatometry results, the microstructure evolution of the ternary alloy was anticipated by thermodynamic calculations performed using the Thermo-Calc version N software[7] and a database containing the descriptions of the Co-Cr-C system and its sub-systems[8-13].

## RESULTS AND DISCUSSION

### As-cast microstructures of the two alloys

The initial microstructures of the two alloys are illustrated by two SEM micrographs at two different magnifications (x250 and x1000) in Figure 1 for the Co-30Cr-0.3C alloy and in Figure 2 for the Co-30Cr-0.3C-4.5Ta alloy. The as-cast ternary alloy is composed of a dendritic matrix of cobalt solid solution and of chromium carbides in the interdendritic spaces. These carbides, darker than matrix when observed in Back
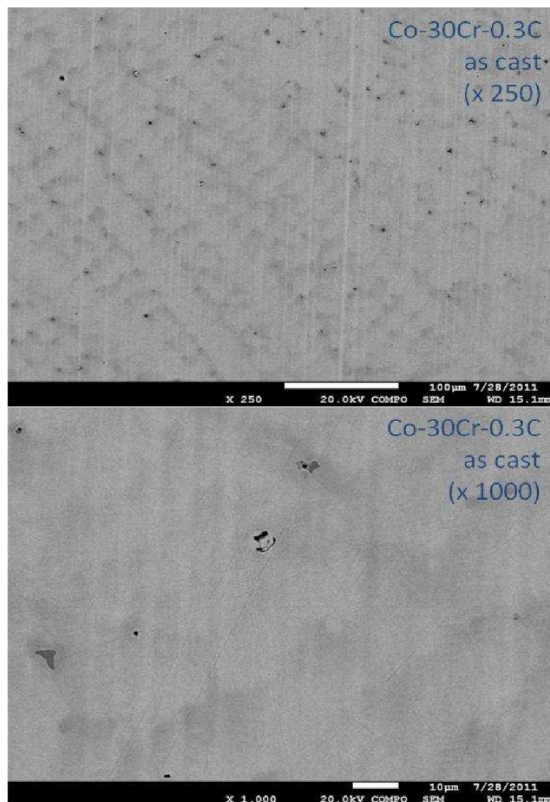
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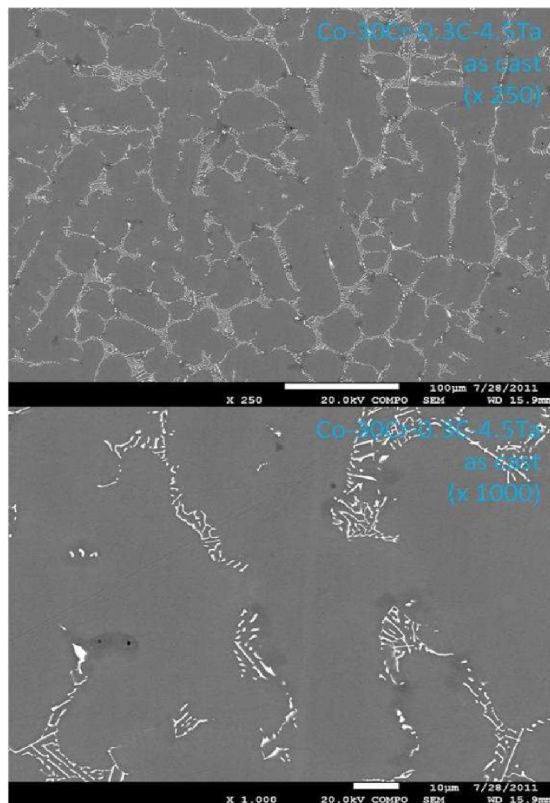**Figure 1 : As-cast microstructure of the Co-30Cr-0.3C alloy at × 250 (top) and × 1000 (bottom)**



**Figure 2 : As-cast microstructure of the Co-30Cr-0.3C4.5Ta alloy at × 250 (top) and × 1000 (bottom)**

Scattered Electrons mode, because of their lower average atomic number, are present in rather low surface fraction. Carbides are much more present in the quaternary alloy, even if its carbon content is the same as the one of the previous alloy, thanks to the stringer carbide-forming character of tantalum. These tantalum carbides (TaC), appearing in white in the same BSE mode because of their average atomic number higher than for matrix, effectively display higher surface fractions. Their position in the interdendritic spaces, as well as their script-like shapes, clearly shows their eutectic character.

**Dilatometry runs**

The deformations which were recorded during the dilatometry runs are plotted versus temperature, for the Co-30Cr-0.3C alloy in Figure 3 when heated to 1050°C, Figure 4 when heated to 1150°C and Figure 5 when heated to 1200°C, and in Figure 6 for the Co-30Cr-0.3C-4.5Ta alloy heated to 1250°C. In these figures the three cycles (heating part + cooling part) are presented separately for the three first graphs, and superposed for the fourth graph.

For the Co-30Cr-0.3C alloy and the targeted stage temperature of 1050°C (Figure 3) the thermal expansion is quite regular, with however some very small discontinuities near 300-400°C and 700-800°C (in the two cases: little stationarity maybe revealing a small contraction compensating the thermal expansion), and the three cycles of thermal deformation are almost superposed.

For the same alloy and the targeted stage temperature of 1150°C (Figure 4) the dilatometry curves are regular and superposed again. Small differences exist with the previous curves: a little discontinuity rather near 500-600°C than 300-400°C for the 1050°C-tests, which is seemingly due to a small additional expansion. Another difference is a slightly enhance dimensional variation during the isothermal stage.

For the Co-30Cr-0.3C alloy again but for a targeted temperature of 1200°C (Figure 5), the good regularity and almost linear character is observed another time, with also sensible dimensional variations during the high temperature isothermal stage.

The results concerning the Co-30Cr-0.3C-4.5Ta alloy cycling between room temperature and 1250°C

with the same parameters of time and heating & cooling rate as for the dilatometry tests of the ternary alloy, are very different. The thermal expansion during the heating part of the first cycle is much more perturbed, with a first discontinuity near 100-200°C and, more important,

a sudden expansion acceleration starting near 1100°C and going on until reaching the targeted temperature. The sample thickness also varies during the 1250°C-stage. The cooling part of the first cycle is also particularly perturbed, with curious dimensional
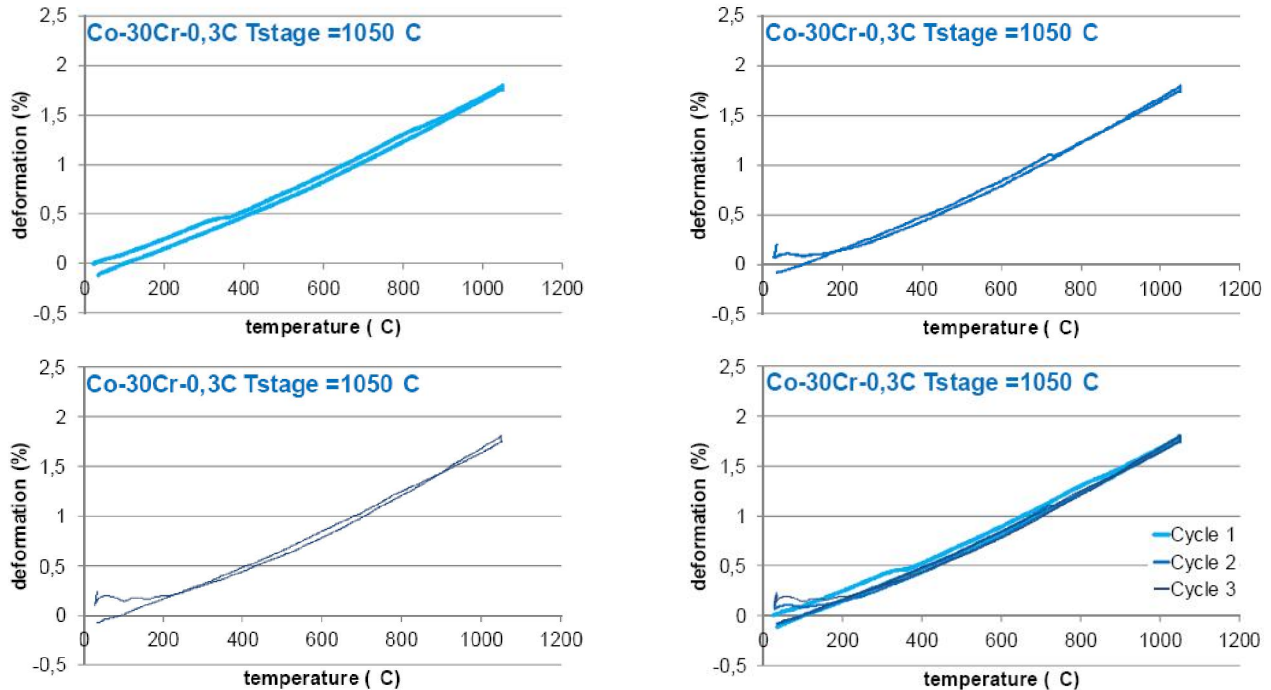


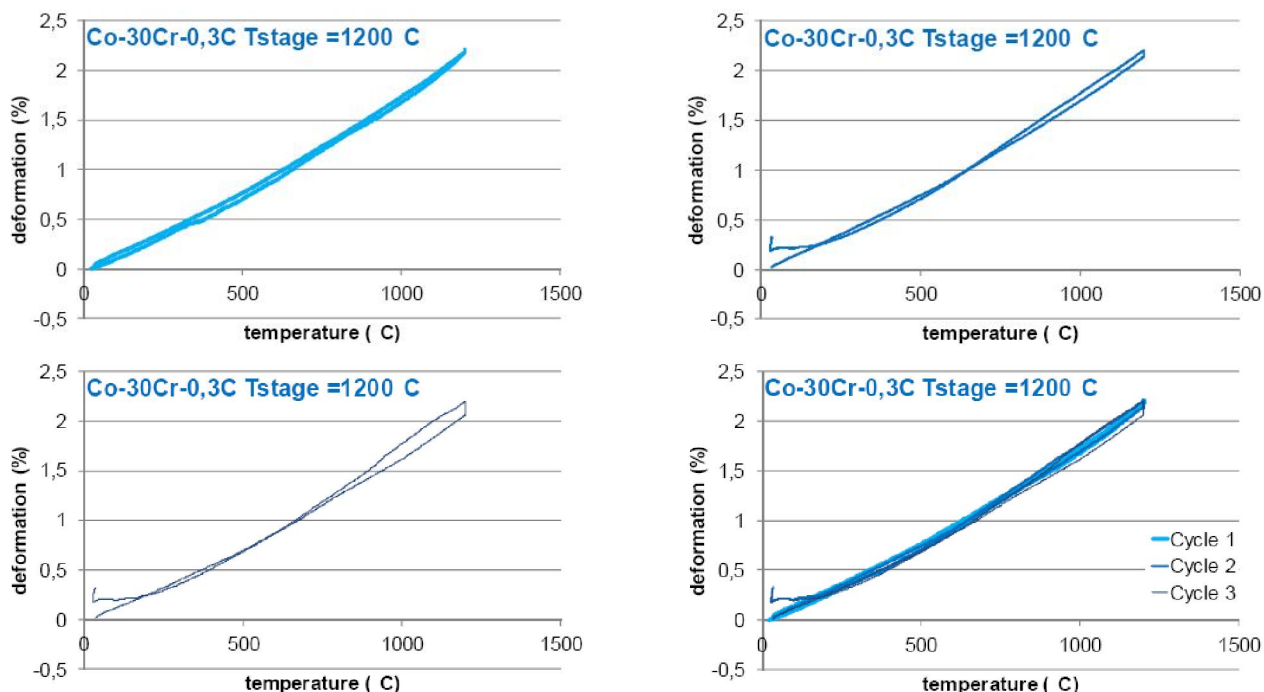(cycle 1: top-left, 2: top-right, 3: bottom-left, the three cycles superposed: bottom-right)

**Figure 3: Dilatometry curves recorded during the three cycles for Co-30Cr-0.3C and 1050°C**
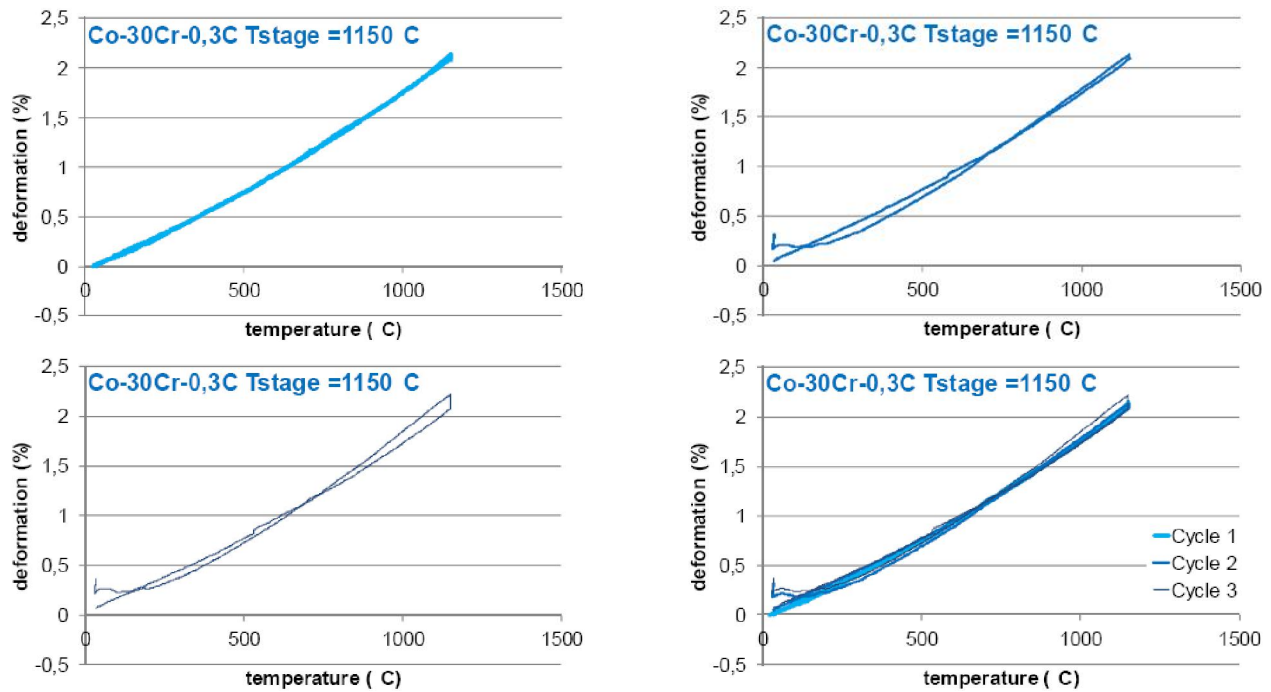


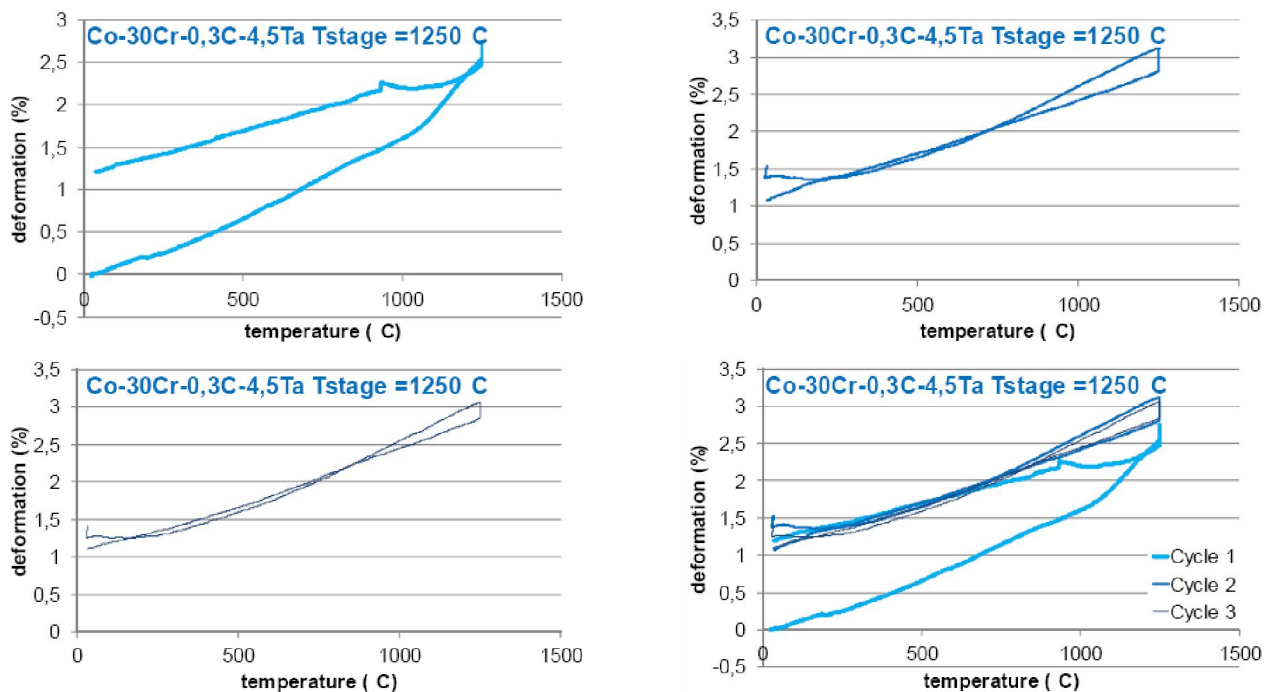(cycle 1: top-left, 2: top-right, 3: bottom-left, the three cycles superposed: bottom-right)

**Figure 4 : Dilatometry curves recorded during the three cycles for Co-30Cr-0.3C and 1150°C**

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(cycle 1: top-left, 2: top-right, 3: bottom-left, the three cycles superposed: bottom-right)

**Figure 5 : Dilatometry curves recorded during the three cycles for Co-30Cr-0.3C and 1200°C**



(cycle 1: top-left, 2: top-right, 3: bottom-left, the three cycles superposed: bottom-right)

**Figure 6 : Dilatometry curves recorded during the three cycles for Co-30Cr-0.3C-4.5Ta and 1250°C**

variations finally resulting in an important positive residual deformation after return to room temperature.

The results of a basic quantitative analysis of the heating parts of the previous curves are presented in TABLE 1. Concerning the ternary alloys it appears that the heating parts of the thermal expansion curves, whatever the considered cycle and the targeted temperature, can be divided in two main parts:
- a first - "slow-expansion" - one starting at a temperature varying in the [220-360°C] range and

finishing at temperature varying in the [610-720°C] range, over which the average thermal expansion coefficient is about 16-20 × 10⁻⁶ K⁻¹,

- a second – "faster expansion" – one starting at the end of the previous part and finishing at the targeted temperature whatever its value, over which the average thermal expansion coefficient is higher: 21.5-24.5 × 10⁻⁶ K⁻¹.

**TABLE 1 : Average thermal expansion coefficients (× 10⁻⁶ K⁻¹) determined on the heating parts**

| Alloy (targeted temperature) | N° of cycle | $T_1$ | $alpha_{T1-T2}$ | $T_2$ | $alpha_{T1-T2}$ | $T_3$ | $alpha_{T1-T2}$ | $T_4$ |
|---|---|---|---|---|---|---|---|---|
| Co-30Cr -0.3C (1050°C) | 1 | Room T. | | 17.3 | | 1050°C | / | / |
| | 2 | 264°C | 17.2 | 612°C | 22.4 | 1050°C | / | / |
| | 3 | 222°C | 15.7 | 639°C | 23.1 | 1050°C | / | / |
| Co-30Cr -0.3C (1150°C) | 1 | Room T. | | 18.5 | | 1150°C | / | / |
| | 2 | 316°C | 19.0 | 686°C | 22.7 | 1150°C | / | / |
| | 3 | 355°C | 19.9 | 722°C | 24.4 | 1150°C | / | / |
| Co-30Cr -0.3C (1200°C) | 1 | Room T. | | 18.0 | | 1200°C | / | / |
| | 2 | 248°C | 16.9 | 624°C | 21.7 | 1200°C | / | / |
| | 3 | 338°C | 17.9 | 667°C | 23.0 | 1200°C | / | / |
| Co-30Cr -0.3C-4.5Ta (1250°C) | 1 | 281°C | 18.6 | 850°C | 19.0 | 1070°C | 43.5 | 1250°C |
| | 2 | 371°C | 14.5 | 696°C | 21.3 | 1020°C | 20.8 | 1250°C |
| | 3 | 322°C | 15.4 | 752°C | | 21.2 | | 1250°C |

The dilatometric records are also plotted versus time in Figure 7, Figure 8 and Figure 9 for the Co-30Cr-0.3C alloy heated to 1050, 1150 and 1200°C respectively, and in Figure 10 for the Co-3Cr-0.3C-4.5Ta heated to 1250°C. In each case the three cycles are represented together (superposed), and the top graph gives a general view of the whole curves and a bottom graph, an enlarged view of the previous one, allowing to better examine the dimensional evolutions during the isothermal stage. It appears for the ternary alloy that the thickness of the samples, increased during the heating, tends to decrease during the isothermal stage, first quickly then slowly as it tends to join a horizontal asymptote, and this for each of the three cycles. Furthermore, the deformation reached at the end of heating tends to be higher for the second cycle than for the first one, and for the third cycle than for the second one, and the rate of isothermal thickness decrease seems to be higher for the third cycle than for the second one and for the second one than for the first one. This is confirmed when the deformation values at the end and at the beginning of the isothermal stage are measured and subtracted to one another to assess the amount of deformation along the whole isothermal stage (TABLE 2). In contrast, the opposite hierarchy is observed between the second and the third cycles of the quaternary alloy (deformation at heating's end and rate of negative isothermal deformation both higher for the second cycle than for the third one). To finish, the residual deformation remaining after return to room temperature, negative for the ternary alloy tested up to 1050°C, and positive for the two other temperatures as well as for the quaternary alloy heated to 1250°C, tends to increase with the stage temperature and to be significantly higher for the quaternary alloy than for the ternary alloy.

### General commentaries

As a first remark one can notice a rather good reproducibility of the thermal expansion during heating of the Co-30Cr-0.3C alloy, between the three cycles and the three temperatures of isothermal stage since the curves were generally well superposed. Among the small perturbations, the ones which occurred at the two levels of temperature [300-400°C]/[500-600°C] on the left hand, and [700-800°C] on the right hand, may be explained by the phase transformations predicted at these levels of temperature by Thermo-Calc calculations, even if these ones allow more knowing the thermodynamic equilibria at given temperature than the dynamic microstructure changes when the temperature rises. The graph representing the evolution

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of nature and mass fraction of phases versus temperature, given in Figure 11, effectively shows that matrix changes can be expected near 300°C and near 800°C (the classical cobalt-chromium matrix change between HCP at low temperature and FCCC at high temperature). For the dimensional variations observed during the 2 hours - isothermal stages at high temperature, one can first suppose that the stresses accumulated in the matrix and in the carbides play a role, as previously noticed in earlier works[5,6,14]. But it is also possible that microstructure changes occurring during the 2 hours spent at high temperature may influence the dimensional stability. The samples were thus examined by electron microscopy after metallography preparation. SEM micrographs of the ternary alloy after the three cycles performed per value of stage temperature and of the quaternary alloy after the three cycles done for 1250°C are displayed in Figure 12. One can see that the microstructures of these two alloys have significantly changed: the chromium carbides are less and less present in the Co-30Cr-0.3C alloy when the stage temperature increases, and the ionitial script-like TaC carbides of the Co-30Cr-0.3C-4.5Ta are sensibly fragmented.
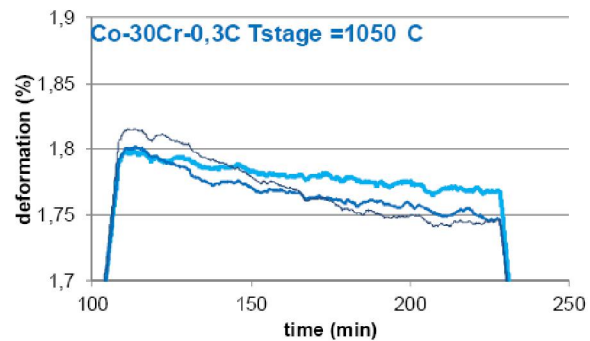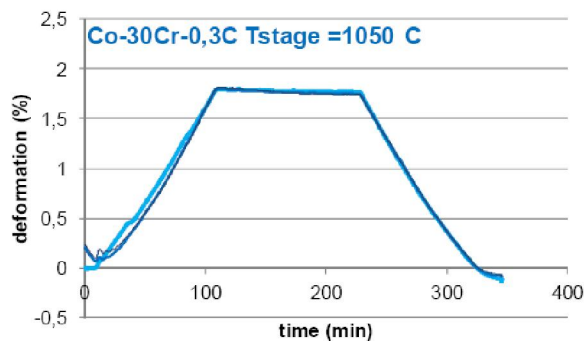


**Figure 7 : Co-30Cr-0.3C – 1050°C: dilatometry results plotted versus time with superposition of the three cycles, in full scale and after enlargement for the stage high temperature part**
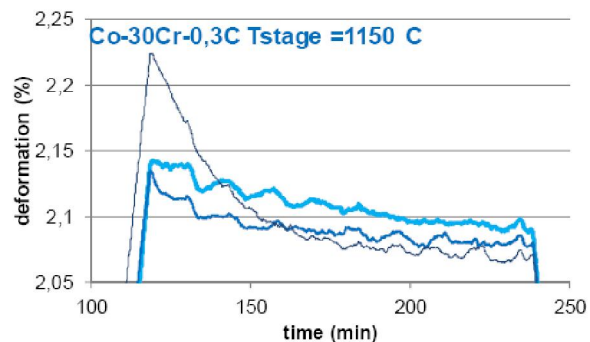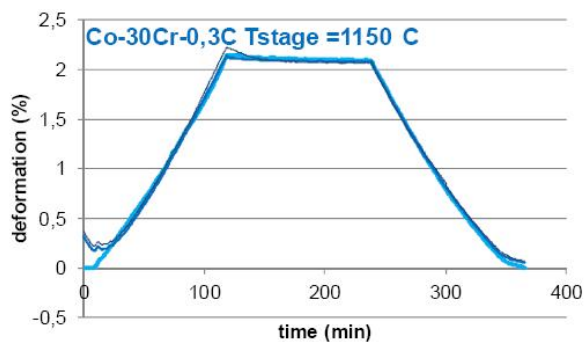


**Figure 8 : Co-30Cr-0.3C – 1150°C: dilatometry results plotted versus time with superposition of the three cycles, in full scale and after enlargement for the stage high temperature part**
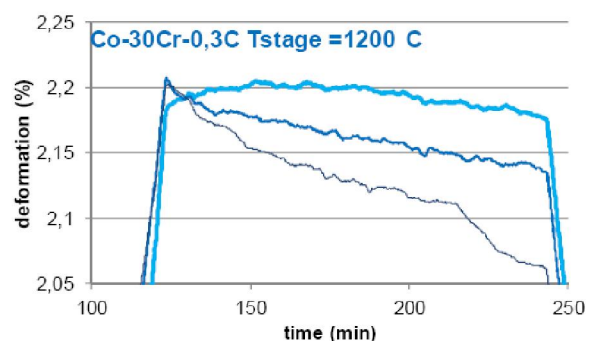


**Figure 9 : Co-30Cr-0.3C – 1200°C: dilatometry results plotted versus time with superposition of the three cycles, in full scale and after enlargement for the stage high temperature part**
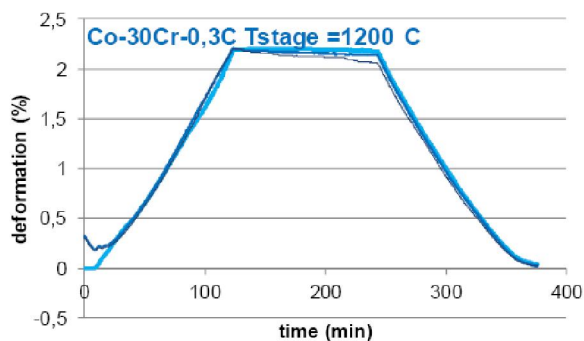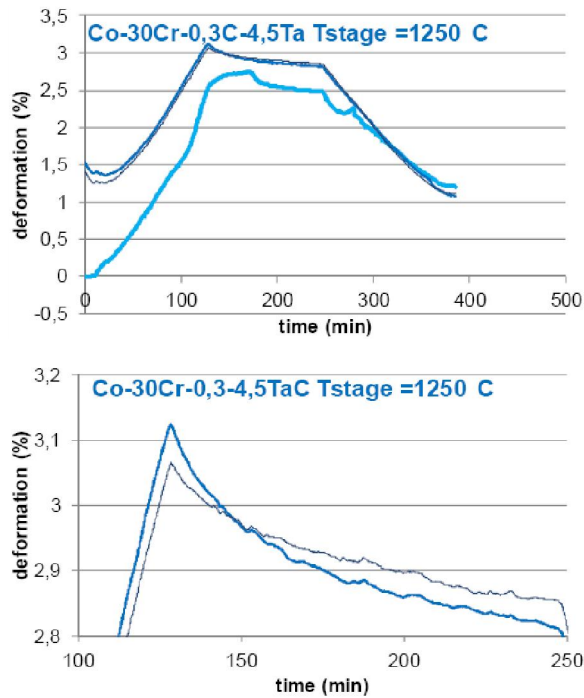
**Figure 10 : Co-30Cr-0.3C-4.5Ta – 1250°C: dilatometry results plotted versus time with superposition of the three cycles, in full scale (top) and after enlargement for the stage high temperature part (bottom)**

**TABLE 2 : Deformations (%) observed at the targeted temperatures**

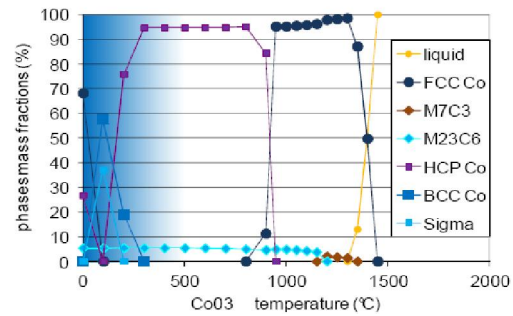| Alloy (targeted temperature) | N° of cycle | epsilon at the beginning of the Isothermal Stage | epsilon at the end of the isothermal stage | delta epsilon achieved during the isothermal stage | Residual delta epsilon observed after return to room temperature (~34°C) |
|---|---|---|---|---|---|
| Co-30Cr -0.3C (1050°C) | 1 | 1.790 | 1.768 | -0.022 | -0.116 |
| | 2 | 1.792 | 1.747 | -0.045 | -0.083 |
| | 3 | 1.804 | 1.745 | -0.059 | -0.071 |
| Co-30Cr -0.3C (1150°C) | 1 | 2.136 | 2.089 | -0.047 | 0 |
| | 2 | 2.134 | 2.078 | -0.056 | +0.048 |
| | 3 | 2.223 | 2.071 | -0.152 | +0.067 |
| Co-30Cr -0.3C (1200°C) | 1 | 2.182 | 2.176 | -0.006 | +0.038 |
| | 2 | 2.207 | 2.135 | -0.072 | +0.024 |
| | 3 | 2.202 | 2.061 | -0.141 | +0.019 |
| Co-30Cr -0.3C-4.5Ta (1250°C) | 1 | 2.563 | 2.482 | -0.081 | +1.204 |
| | 2 | 3.105 | 2.806 | -0.299 | +1.078 |
| | 3 | 3.053 | 2.850 | -0.203 | +1.108 |



**Figure 11 : Evolution of the microstructure state of the Co-30Cr-0.3C at heating up to high temperature, according to Thermo-Calc calculations**
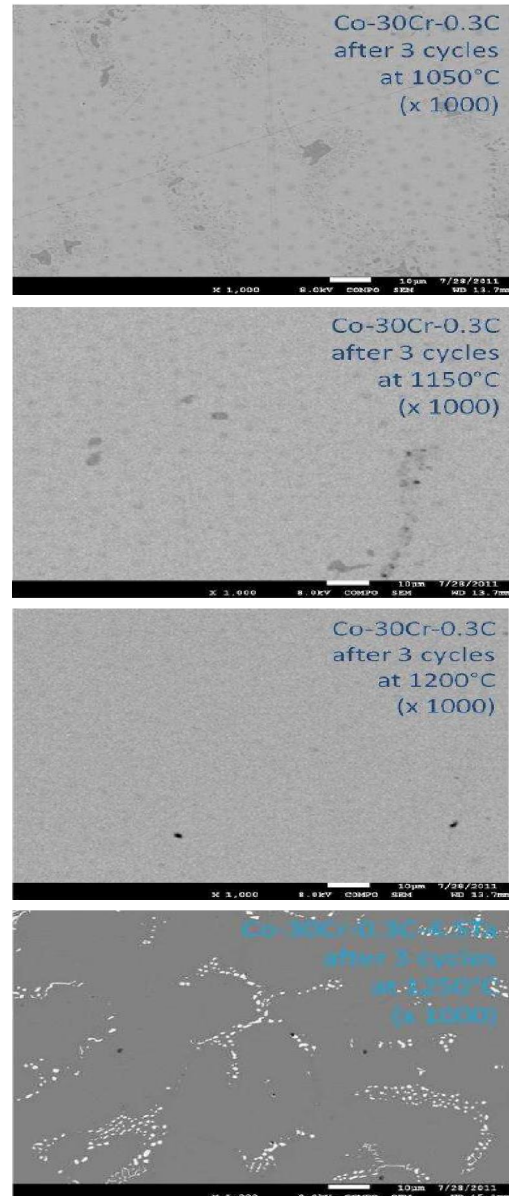


Co-30Cr-0.3C for 1050°C, for 1150°C and 1200°C , and Co-30Cr-03C-4.5Ta

**Figure 12 : Microstructure states of the two alloys after the three cycles of dilatometry run;**

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## CONCLUSIONS

The two carbides-containing cobalt-based alloys studied in this work have shown, in some cases a particular thermal expansion behaviour during heating, but also, in all cases, a problem of dimensional stability at high temperature. This can be due to either the release of thermo-mechanical stresses developed during the thermic variations (heating, or cooling after solidification or at the end of the previous dilatometric cycle), or to microstructure evolutions during the stage, favoured by the high temperature. Such phenomena must to be taken into account since they may lead to problem of dimensional precision in service.

## ACKNOWLEDGEMENTS

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