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# Effects of dendritic orientation and of aging treatment on the thermal expansion of Ni-based and Co-based cast alloys

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## ABSTRACT

Thermal expansion is of great importance for alloys working at high temperature. Both dendrite orientation and morphologies of carbides can influence this property in cast alloys. Two cast alloys, Ni-30Cr-1.0C and Co-8Ni-30Cr-0.5C-7.5Ta (in wt.%), containing high quantities of chromium carbides and of tantalum carbides respectively, were heat treated at 1200°C for durations up to 100 hours. Their thermal expansion behaviours were characterized between room temperature and 1200°C and studied with respect to the dendrite orientation and the heat treatment duration. The thermal expansion is almost linear up to temperatures higher than 1000°C but, in some cases, a contraction applied by carbides on the matrix weakened because of high temperature, occurs before reaching 1200°C and during the isothermal dwell before cooling. The average thermal coefficient is slightly influenced by dendrite orientation and by a more or less long treatment at high temperature before test. The negative deformation of matrix due to carbides, and the permanent contraction kept at the end of experiment, seem being favoured in the dendrite direction in the case of the cobalt alloy. It is less true for the nickel alloy. The coarsening of the $Cr_7C_3$ carbides of the Ni-based alloy and the fragmentation of the TaC carbides of the Co-based alloy, lower both the contraction at high temperature and the resulting permanent deformation.

## KEYWORDS

Cast alloys;
Carbides;
Dendrite orientation;
Aging treatment;
Thermal expansion;
Hardness.

## INTRODUCTION

Solidification of metallic alloys often induces texture heterogeneities in cast pieces[1]. Generally, molten alloys solidify from the mould wall with a first thin layer with very fine and equiaxed microstructure. Thereafter only the crystals which are the best oriented with respect to the local thermal gradient grow inward the ingot. This leads to the development of a “columnar zone” in which solidified columns or dendrites are mainly perpendicular to the external surface of the cast piece (Figure 1). If the thermal gradient in the mushy zone is decreased enough before end of solidification, a third microstructure zone solidifies in the center of the ingot, from nucleus directly appeared in liquid alloy. This new crystals grow without specific orientation with regard to the external surface of ingot and lead to the “equiaxed zone”.

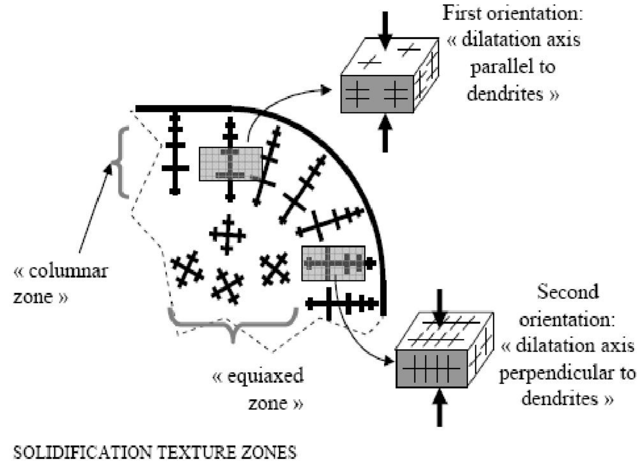

**Figure 1 : Texture of the outer part of a solidified metallic piece and the two main orientations of thermal expansion which can be taken into consideration.**

In the case of cast alloys or superalloys containing eutectic carbides solidified in interdendritic spaces, like carbides-strengthened nickel alloys or cobalt-based superalloys[2-4], the microstructure orientation can lead to an anisotropic mechanical behaviour: tensile strength, creep deformation or thermal expansion[5]. Indeed, on the one hand dendritic orientation induces the same orientation for the interdendritic carbide network, and on the other hand carbides play an important role because of their mechanical properties which are very different with regard to the metallic matrix ones. The possible influence of orientation can also depend on the morphologies of carbides, since it was already observed that as-cast carbides and fragmented carbides (in aged alloys) led to different levels of tensile properties and of thermal expansion[6].

The aim of this work is to study the influence of both dendritic orientation and of carbides fragmentation on the thermal expansion behaviours of a nickel-base alloy highly reinforced by chromium carbides and of a cobalt-based alloy strengthened by tantalum carbides.

## EXPERIMENTAL

### Synthesis and cutting of the studied alloys

The two alloys were elaborated by foundry, using a High Frequency (300kHz) induction furnace (CELES), from pure elements (purity > 99.9%). Melting and solidification took place in the water-cooled copper crucible of the furnace. Three ingots, each of about 100g, were obtained per studied alloy (then six ingots). For each alloy a first one was heated at 20 K × min$^{-1}$ from room temperature up to 1200°C, maintained at this temperature for 5 hours then air quenched. The second one was heated at the same temperature with the same heating rate, but maintained during 25 hours before air quenching. The third one underwent the same type of heat treatment, but with a dwell of 100 hours before air quenching.

All ingots were thereafter cut in order to get a first part for chemical composition analysis and microstructure examination, and secondly two types of parallelepipeds parts as described in Figure 1: about 4mm × 4mm (square main faces) × 2mm (thickness and direction of the studied thermal expansion), for the dilatometry experiments.

### Metallographic characterization

The first cut sample was embedded in a cold {resin + hardener} mixture and this mounted sample was polished with grinding papers from grade 240 to grade 1,200, then ultrasonic cleaned, and mirror-like polished with 1µm alumina suspension. Metallographic examinations were done using a Scanning Electron Microscope (SEM, type: Philips XL30), in Back Scattered Electrons mode (BSE) with an acceleration voltage of 20kV. The chemical composition of each ingot was assessed by microanalysis on the whole alloy, by Wavelength Dispersion Spectrometry (WDS) using a Cameca SX100 microprobe.

### Dilatometry runs and structure examinations / hardness measurements on dilatometry samples

The thermal expansion was measured during the heating from room temperature up to 1200°C (rate of 10 K × min$^{-1}$), the dwell of 600 seconds and the cooling (rate of -10 K × min$^{-1}$). Comparisons between curves were done between the two types of orientation and versus the aging duration at 1200°C initially applied to ingots. The microstructures of the main faces of the dilatometry samples were examined (with the SEM in BSE mode), after they had been used for the thermal expansion measurements and prepared as the metallography samples above, in order to control the dendritic orientations. Vickers indentations with a load of 30kg were performed on the same samples (Testwell Wolpert apparatus) in order to detect an eventual dependence of hardness on dendritic orientation,.

## RESULTS AND DISCUSSION

### Microstructures and chemical compositions of the alloys

For each alloy the chemical compositions of the three ingots obviously well respected the targeted ones, since the measured contents are all in the ranges 30 ±1wt.% for Cr for the two alloys and 7.6 ±0.5wt.% for Ta in the cobalt alloy. Concerning carbon, which cannot be analysed, the obtained carbides densities suggest that it is close to the targeted values, as usually verified by spark spectroscopy for similar alloys previously elaborated following the same procedure.

The microstructures of the six ingots after the different durations at 1200°C are illustrated in Figure 2. The two alloys contain a dendritic matrix with eutectic carbides in the interdendritic spaces. These carbides are $Cr_7C_3$ in the nickel-based alloy and they seem becoming rounder and their surface fractions a little lower when the duration of the aging treatment increases. The carbides in the cobalt-based alloy, which are TaC, are more and more fractioned when the aging duration increases. Their surface fraction also seems slightly decreasing. For the Co-based alloy like for the Ni-based one, the change in volume fraction of carbides is not significant and it can be considered that the main difference is only on the carbides morphology point of view. Typical microstructures for the two orientations are illustrated in Figure 3, in which, for the cobalt-alloy aged during 100 hours at 1200°C, no dendrites are visible in the top micrograph (no primary dendrite axis since they are all cut perpendicularly in this cross section), while they can be easily seen in the bottom micrograph since some primary dendrites axis are cut along their axis.

### Dilatometry measurements

The dilatometric curves obtained for the nickel-based alloy are displayed in Figure 4. They are drawn from 100°C and not from room temperature to allow thermal homogenization of the apparatus before measurement can be done The three graphs correspond to the three metallurgical states (aged during 5h, 25h and 100h at 1200°C), and each of them contains the whole curve (heating + cooling) for the two orientations. Generally thermal expansion acted continuously from 100°C up to 1200°C, but sometimes only up to several tens Celsius degrees before 1200°C. Indeed, a lowering of thermal expansion, and even a contraction in some cases, can be noticed at the end of heating. This occurs for the two dendritic orientations for the alloy aged 5 hours, and affects only one of the orientations for the two longest aging durations. In the cases where this phenomenon occurred, the new thickness of the sample after cooling is lower than before experiment. The curves

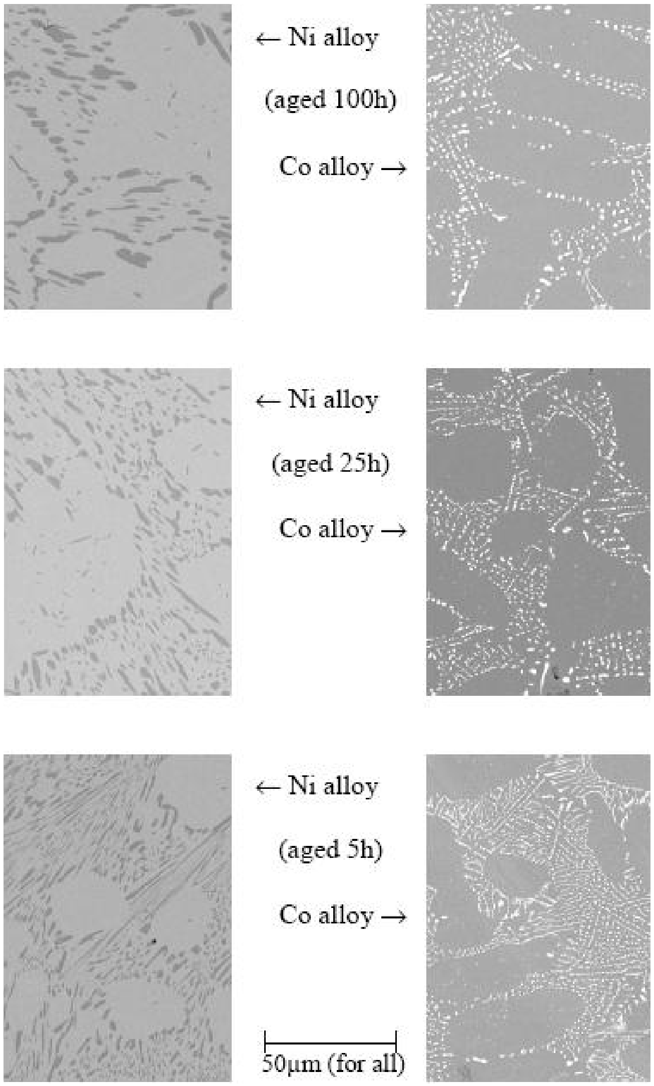

**Figure 2 : Microstructures of the obtained alloys (SEM in BSE mode)**

obtained for the cobalt-based alloy are shown in Figure 5. The same commentaries as above can be done. However, it can be noticed that the contraction at the end of heating seems, for this alloy, existing only for the two lowest aging durations and only for the parallel orientation.

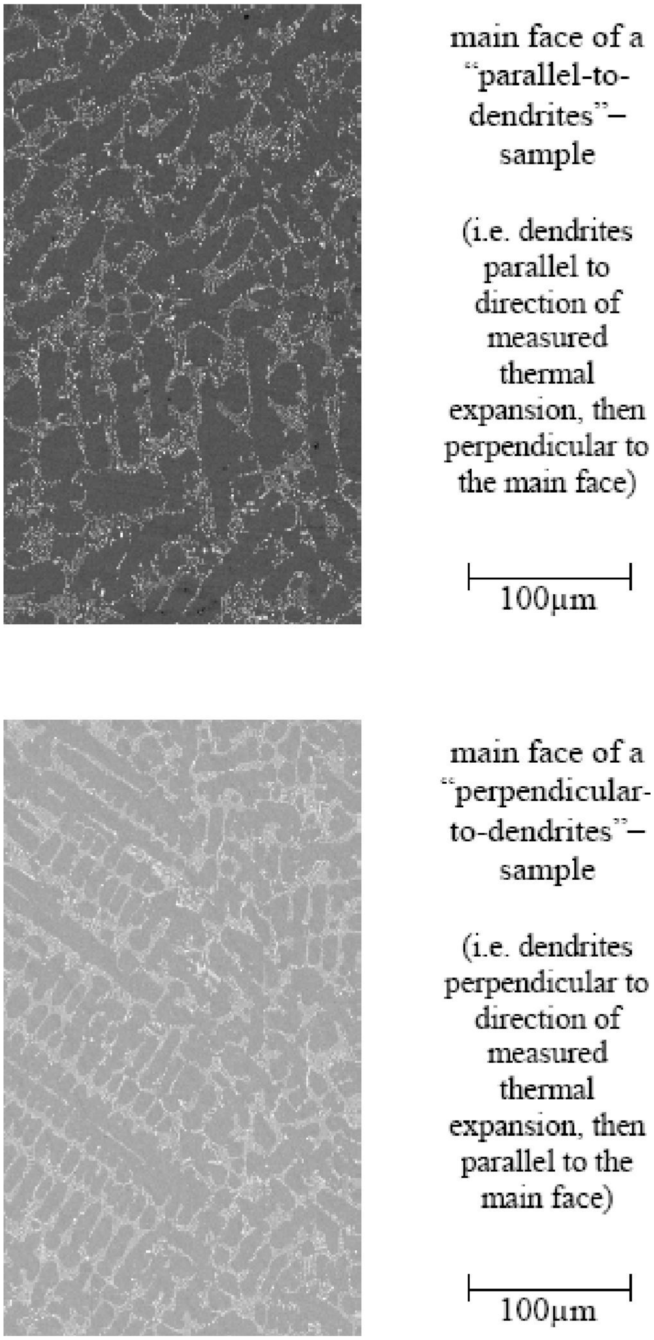

**Figure 3 : Typical microstructures (SEM/BSE) of the main faces of the two types of sample for thermal expansion measurements (here: the cobalt-based alloy aged during 100 hours at 1200°C)**

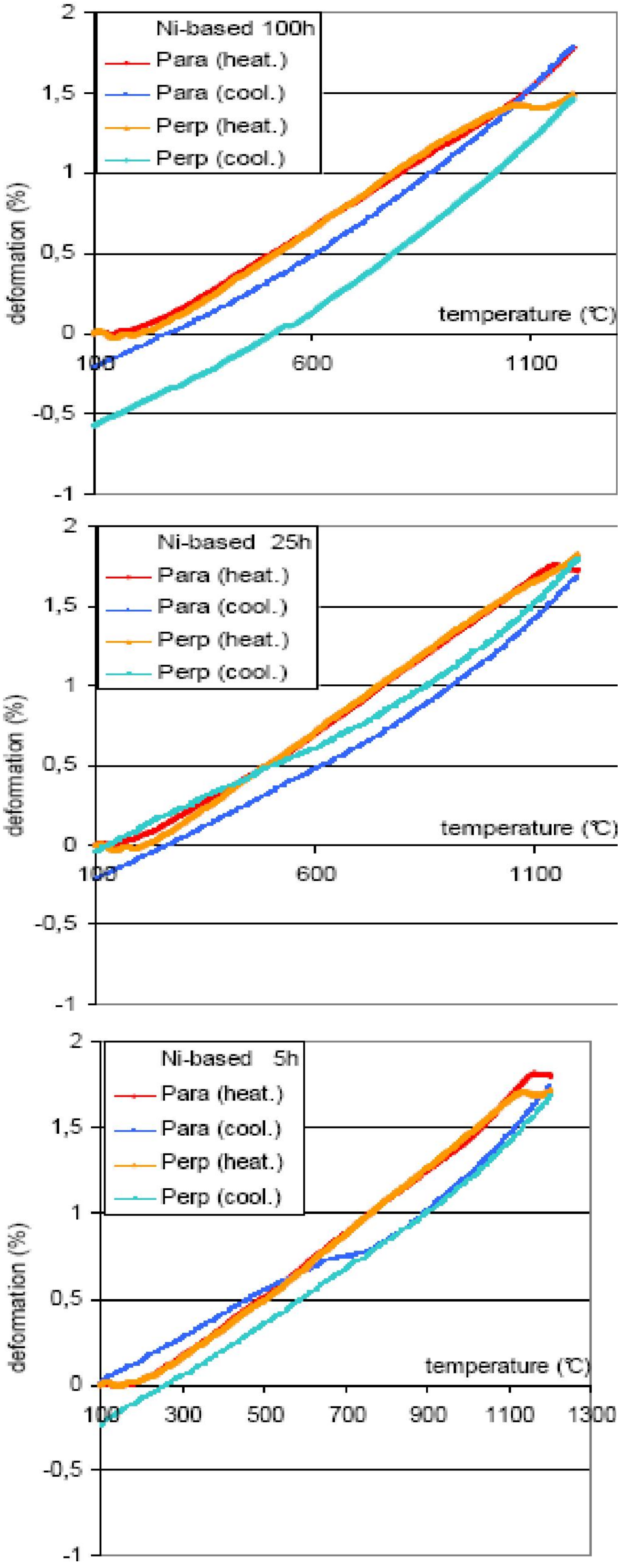

**Figure 4 : Dilatometry curves (heating part + cooling part) of the Ni-30Cr-1.0C alloy for the three aging durations at 1200°C and the two orientations**

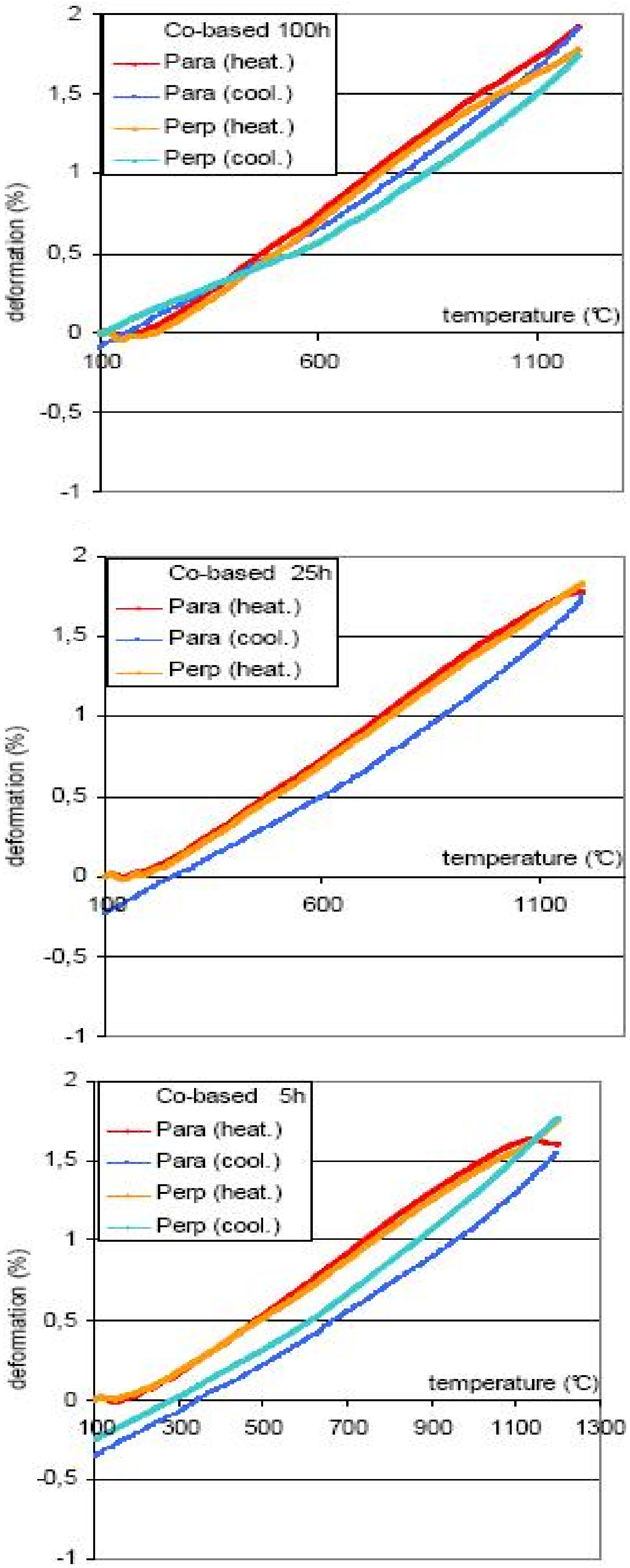

**Figure 5 : Dilatometry curves (heating + cooling parts*) of the Co-8Ni-30Cr-0.5C-7.5Ta alloy for the three aging durations and the two orientations** (*: except for 25h because of a problem occurred at cooling)

**TABLE 1 : Average values of the thermal expansion coefficient in the most linear part of the heating dilatometry curves for the two alloys and the three aging treatments**

| | **Ni-based alloy** | |
|---|---|---|
| **(temperature range)** | **parallel** | **perpend.** |
| aged 100h | 17.1<br>(300-1100°C) | 18.2<br>(300-1000°C) |
| aged 25h | 18.7<br>(300-1100°C) | 19.4<br>(250-900°C) |
| aged 5h | 18.1<br>(300-1100°C) | 19.1<br>(300-1100°C) |
| | **Co-based alloy** | |
| **(temperature range)** | **parallel** | **perpend.** |
| aged 100h | 19.6<br>(200-1200°C) | 20.2<br>(300-1000°C) |
| aged 25h | 19.1<br>(300-1100°C) | 18.7<br>(300-1200°C) |
| aged 5h | 19.1<br>(300-1000°C) | 18.1<br>(300-1000°C) |

The curves were exploited and the obtained thermal coefficients determined on the most linear part of the heating dilatometry curves are displayed in TABLE 1 for the two alloys (the temperature range of measurement is given under each coefficient). The thermal expansion coefficient of the Ni-based alloy seems being lower for the parallel orientation than for the perdendicular one in all cases, and it increases between 5h and 25h of aging, then decreases between 25h and 100h of aging, for the two orientations.

In contrast, for the Co-based alloy, the coefficient of thermal expansion, which is almost the same for the two orientations, seems increasing when the aging duration increases.

TABLE 2 and TABLE 3 show the results of a more detailed analysis of the curves, since the thermal expansion coefficients did not represent the total thermal expansion behaviour of these alloys. Several new characteristics of these ones were then considered:

(1) the final dilatation really obtained when temperature reached 1200°C, called “dilat. end heat.”

(2) the total relative deformation when reaching 1200°C due to contraction, called “def. end heating”; this was assessed by the difference of, on the one hand the theoretic dilatation which would be obtained in absence of any contraction (extrapolation to 1200°C of the not deformed part of the curve), and of the other hand the “dilat. end heat.”

(3) the contraction occurred during the 600 seconds

**TABLE 2 : Data measured on the dilatation curves of the nickel-based alloy**

| **Ni-based alloy** | **100h** | |
|---|---|---|
| orientation | parallel | perpend. |
| [1]dilat. end heat. | 1.79% | 1.49% |
| [2]def. end heating | > 1200°C<br>≈ 0 | > 1082°C<br>≈ - 0.11% |
| [3]def. end dwell | ≈ 0% | - 0.03% |
| [4]sum of the two upper lines | ≈ 0% | - 0.14% |
| [5]remaining def. at 300°C | - 0.13% | - 0.45% |
| **Ni-based alloy** | **25h** | |
| orientation | parallel | perpend. |
| [1]dilat. end heat. | 1.72% | 1.82% |
| [2]def. end heating | >1149°C<br>≈ - 0.23% | > 1200°C<br>≈ 0 |
| [3]def. end dwell | - 0.04% | + 0.02 |
| [4]sum of the two upper lines | - 0.27% | +0.02% |
| [5]remaining def. at 300°C | - 0.15% | + 0.09% |
| **Ni-based alloy** | **5h** | |
| orientation | parallel | perpend. |
| [1]dilat. end heat. | 1.79% | 1.71% |
| [2]def. end heating | >1163°C<br>≈ - 0.19% | >1146°C<br>≈ - 0.14% |
| [3]def. end dwell | - 0.05% | - 0.03% |
| [4]sum of the two upper lines | - 0.24% | - 0.17% |
| [5]remaining def. at 300°C | + 0.10% | - 0.11% |

spent at 1200°C, called “def. end dwell”

(4) sum of the two values of (2) and (3), which represents the total contraction occurred between the appearance of the phenomenon (near the end of heating) and the dwell’s end

(5) the residual deformation at 300°C, i.e. difference between dilatation at 300°C in the cooling part and dilatation at 300°C in the heating part of the dilatometric curve (this temperature was chosen high enough to avoid dilatometric problems specific to very low temperatures, and low enough to take into account all deformations occurred at medium and high temperatures).

The dilatation at the end of heating (1) is very variable for the Ni-based alloy (TABLE 2) and the lowest values clearly correspond of the existence of contraction at the end of heating. This one led to deformations at the end of heating (2) which tend to be higher for the shortest aging durations than for the longest ones. Contraction seemed go on during the ten minutes spent at 1200°C before cooling, here too more for the parallel orientation than for the perpendicular one. These contractions at the end of heating, during the dwell at 1200°C, and maybe also at the beginning of cooling, led to cooling parts of the dilatometry curves which are significantly bellow the heating parts. This is not always found again when the sum of the two upper lines (4) is compared to the remaining deformation at 300°C (5) since other phenomena can act during cooling (e.g. cooling part of the curve for the parallel orientation for the Ni-based alloy aged during 5h). But, one can consider that there is generally a good qualitative correspondence.

The dilatations at the end of heating (1) are generally higher for the Co-based alloy (TABLE 3) than for the Ni-based one. There are no deformation at the end of heating (2), excepted for the parallel orientation after aging during 5 hours only, and the deformation during the 10 minutes–dwell at 1200°C (3) is lower than for the nickel alloy, in all cases. The sum of deformations (4), as well as the deformation remaining at 300°C (5) are generally closer to zero than for the nickel alloy.

## Hardness measurements

After all dilatometric experiments, the parallel-type and perpendicular-type samples were embedded in resin and polished until the mirror-like surface state was obtained. They were etched by the Groesbeck solution (4g $KMnO_4$ and 4g NaOH in 100mL of distilled water) in order to reveal the general microstructures for a better easiness of the hardness tests. Three Vickers indentations (load: 30kg) were performed in each sample, and the obtained average values and standard deviation values (taken as uncertainty) are graphically given in Figure 6. In the latter it clearly appears that, despite a carbon content lower than in the Ni-based alloy, the Co-based alloy is significantly harder than the latter (almost 100 Vickers units more for all sets of {orientation, aging duration} conditions). The average hardness decreases when the aging duration increases, especially between 5 hours and 25 hours. The perpendicular-type sample seems to be harder than the parallel-type one in the case of the Co-based alloy, while it would be the contrary for the Ni-based alloy.

**TABLE 3 : Data measured on the dilatation curves of the cobalt-based alloy**

| Co-based alloy | 100h | |
|---|---|---|
| orientation | parallel | perpend. |
| [1]dilat. end heating | 1.92% | 1.78% |
| [2]def. end heating | > 1200°C<br>≈ 0 | > 1200°C<br>≈ 0 |
| [3]def. end dwell | ≈ 0% | - 0.03% |
| [4]sum of the two upper lines | ≈ 0% | - 0.03% |
| [5]remaining def. at 300°C | + 0.04% | + 0.11% |

| Co-based alloy | 25h | |
|---|---|---|
| orientation | parallel | perpend. |
| [1]dilat. end heating | 1.77% | 1.83% |
| [2]def. end heating | > 1200°C<br>≈ 0 | > 1200°C<br>≈ 0 |
| [3]def. end dwell | - 0.01% | + 0.14% |
| [4]sum of the two upper lines | - 0.01% | + 0.14% |
| [5]remaining def. at 300°C | - 0.14% | + 0.52% |

| Co-based alloy | 5h | |
|---|---|---|
| orientation | parallel | perpend. |
| [1]dilat. end heating | 1.60% | 1.76% |
| [2]def. end heating | > 1089°C<br>≈ - 0.20% | > 1200°C<br>≈ 0 |
| [3]def. end dwell | - 0.06% | 0 |
| [4]sum of the two upper lines | - 0.26% | 0 |
| [5]remaining def. at 300°C | - 0.25% | - 0.17% |

## General commentaries

The microstructure anisotropy resulting from the solidification direction not far from the external surface of the ingot was observed on the main faces of the samples obtained by special cutting, thanks to the contrasted micrographs allowed by the presence of a grey matrix with a darker (chromium carbides in the nickel alloy) or on the contrary whiter (tantalum carbides in the cobalt alloy) second phase present in the interdendritic spaces. However, it was obvious that each cross-section was a mix of dendrites parallel or perpendicular, with only a predominance of dendrites mainly oriented either parallel to the studied dilatation direction or perpendicular.

Nevertheless, there are significant consequences of this microstructure anisotropy on the thermal expansion behaviour. This was first seen with the slight differences of thermal coefficients, but it was more obvious with the phenomena occurring at the end of heating and during the dwell at 1200°C before cooling, and probably also at the beginning of cooling when temperature was still high enough. Indeed, in such alloys rich in carbides, thanks to the high carbon content in the nickel alloy and to the strong carbide-forming power of tantalum in the cobalt alloy, the dilatation difference between carbides ($10.6 \times 10^{-6}$ $K^{-1}$ for $Cr_7C_3$ and $6.3 \times 10^{-6}$ $K^{-1}$ for TaC[7]) leads to a compressive stress applied by carbides on matrix when temperature has become high enough to sufficiently weaken the creep-resistance of the latter[5]. This contraction seems being favoured for samples in which dendrites are mainly parallel to the studied direction, in the case of the Co-based alloy, which is probably due to a better continuity of the carbides network in this direction. This was already seen in a previous work[5] concerning the effect of dendrite orientation on the thermal expansion of a Ni-free Co-based alloy strengthened by a high density of chromium carbides. In the case of the Ni-based alloy, the difference of thermal expansion near the end of heating was less systematic between the two orientations, since similar contractions were seen for the two orientations after a 5h-aging, while contraction affected either the perpendicular orientation after a 25h-aging (i.e. like a not aged Ni-30Cr-0.8C alloy[5]) or the parallel

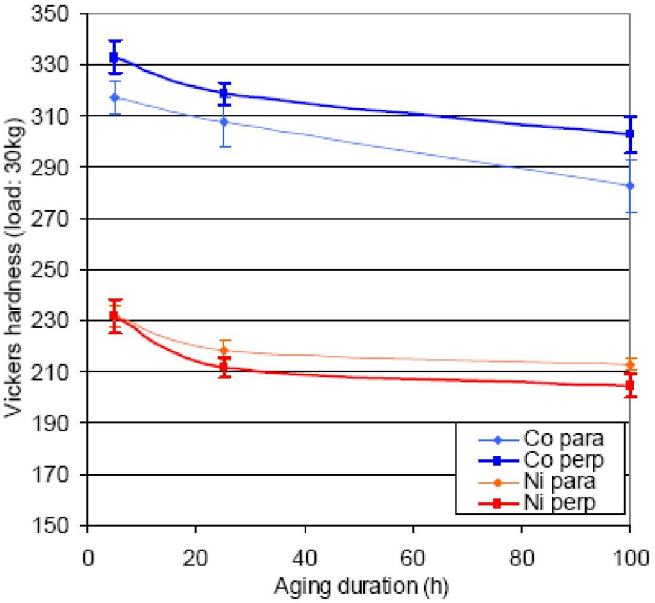

**Figure 6 : Hardness of the two alloys for the two orientations and for the two aging treatments**

orientation after a 100h-aging.

An aging at 1200°C leads to significant modifications of the carbide network: mainly a coarsening of the chromium carbides in the nickel alloy and a fragmentation of the tantalum carbides in the cobalt alloy. For the cobalt alloy, the influence of fractioned TaC carbides on the matrix is significantly decreased, with consequently a slight increase in thermal expansion coefficient for the two orientations and the progressive disappearance of the contraction at the end of heating when the aging duration increases. For the nickel alloy, the coarsening of carbides also modifies the thermal expansion behaviour but in a way which is not so clear, probably because of the higher volume fraction of carbides due to the carbon content which is twice the Co-based alloy's one. A so high volume fraction of carbides may lead to an interconnection which is less dependent on the dendrite orientation than for lower carbon content, which allows a contraction in all directions at high temperature. After coarsening due to aging at high temperature, the influence of carbides should remain, more or less, with only little influence of dendrite orientation.

The decrease in hardness at room temperature can be directly related to the carbides morphology. The coarsening of chromium carbides in the nickel alloy, as well as the fragmentation of the tantalum carbides in the cobalt alloy, lead to lower hardness because of the loss of continuity for the carbides network.

## CONCLUSIONS

The dendrite orientation of metallic cast pieces containing a high fraction of carbides is to be taken into account when the thermal expansion behaviour is of high importance. This is especially true for the permanent deformation which can result from heating up to very high temperatures because of viscous-plastic deformation of matrix under compressive stresses applied by carbides. The consequences for the thermal expansion coefficient at not so high temperatures are less important. If keeping reversibility for the thermal deformation is necessary, the fragmentation of carbides by high temperature treatment can help to resolve this problem, and also allows a decrease in room temperature hardness which can also depend on dendrite orientation.

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