Academic Journal of Chemistry
ISSN(e): 2519-7045, ISSN(p): 2521-0211
Vol. 5, Issue. 3, pp: 17-24, 2020
URL: https://arpgweb.com/journal/journal/20
DOI: https://doi.org/10.32861/ajc.53.17.24

Academic Research Publishing Group

Original Research **Open Access**

Thermal Expansion and Microstructure Behavior at Elevated Temperature of various {Ni, Co}-based Cast Superalloys

Patrice Berthod (Corresponding Author)
Université de Lorraine, CNRS, IJL, F-54000 Nancy, France
Email: patrice.berthod@univ-lorraine.fr

Jean-Paul Gomis
Université de Lorraine, FST, F-54500 Vandoeuvre-lès-Nancy, France

Lionel Aranda
Université de Lorraine, CNRS, IJL, F-54000 Nancy, France

Pierre-Jean Panteix
Université de Lorraine, CNRS, IJL, F-54000 Nancy, France

Article History
Received: February 12, 2020
Revised: March 10, 2020
Accepted: March 16, 2020
Published: March 19, 2020

Abstract

This paper aims to investigate the thermal expansion behavior, up to an elevated temperature, of superalloys based on nickel and cobalt with various proportions and designed to be strengthened by tantalum carbides. The as-cast microstructures of these superalloys and their evolutions at two very high temperatures were also of interest. All results are discussed by considering the Ni/Co repartition in the base element position. It appears that when the Ni content is higher than the Co one: 1/the thermal expansion is slower, 2/the as-cast microstructures as well as the ones stabilized at high temperature contain not only TaC but also chromium carbides, and 3/the hardness in as-cast or aged state is lower.

Keywords: Superalloys; Nickel and cobalt; High temperature; Microstructure; Thermal expansion.

1. Introduction

Superalloys with a polycrystalline structure and hardened by carbides exist since the middle of the last century [1]. Even advanced superalloys appeared during the last decades, such as Oxide Dispersion Strengthened (ODS) superalloys produced by powder metallurgy (PM) and mechanical alloying (MA) and Ni-based single-crystals resulting from the directional growth of a selected unique grain [2], these traditional superalloys stay good solutions for many needs: high temperature applications requiring isotropic behavior and manufacturability of compact components. Equi–axed polycrystalline superalloys reinforced by MC carbides are especially efficient for service on long term at elevated temperatures. Commercial nickel–based superalloys contain such carbides for this purpose, as either equi–axed alloys [3, 4] or directionnaly solidified alloys [5]. Some industrial cobalt–based alloys are also strengthened by MC carbides, notably tantalum carbides. These ones may be themselves either polycrystalline and equi–axed [6-8] or directionally solidified [9]. Many superalloys with polycristalline and equi–axed microstructures are also resistant against high temperature oxidation and corrosion thanks to the presence of several tens weight percent of chromium in their chemical composition [10, 11]. The presence of so high contents in this second carbide-former element may provoke some troubles in the formation of tantalum monocarbides TaC which, consequently, can be not the single carbide phase present despite atomic contents in Ta and in C especially chosen to favor TaC carbides. Oviously the competition between tantalum and chromium in the carbide formation depends on the metallic environment of tantalum, chromium and carbon: for 25 to 30wt.%Cr present, tantalum carbides are favored in cobalt-based alloys [12] while carbon is shared by tantalum and chromium in nickel-based alloys [13]. Since many cobalt-based alloys also contain nickel (for stabilizing the Face Centred Cubic crystalline network of the matrix, for instance) and some nickel-based alloys contain also small amounts of cobalt (for reinforcing the matrix by solid solution hardening, for instance), it can be interesting to explore the effect, on its microstructure and properties, of a regular enrichment in cobalt of a {Ta, C, Cr}–containing nickel alloy base, up to obtaining the corresponding cobalt alloy. This is was undertaken in this work for a {6Ta, 0.4C, 25Cr; wt.%}-containing Ni-base alloy, especially devoted to the as-cast microstructures, microstructures stabilized at two very high temperatures, and to the thermal expansion behavior up to the highest of these temperatures.

2. Materials and Methods

This work concerns a series of alloys presenting a same carbide–forming configuration {6Ta, 0.4C, 25Cr; wt.%} and difference balances between nickel and cobalt from only nickel to only cobalt, and different Ni-Co combinations between. They were synthesized as ingots weighing about 40 grams and prepared from pure elements (Ni, Co, Ta, C-graphite and Cr from Alfa Aesar, purities all > 99.9%). The foundry technique was high frequency induction melting (110kHz, 4kV) under inert atmosphere (300mbars of pure Ar). Each ingot was cut, using a metallographic saw, to obtain a sample for the examination of the as-cast microstructure, two samples to expose to two high temperatures for long times, and a sample to perform high temperature dilatometry.

Per alloy, two samples were exposed, in a high temperature resistive furnace, one to 1200°C for 70 hours and one to 1250°C for 170 hours, preceded in both cases by a heating at 20°C min^{-1} and finished by a cooling at 10°C min^{-1}.

The sample remain in the as–cast state and the two samples aged at high temperature were all embedded in a cold resin mixture, ground and polished until obtaining a mirror-like surface state allowing metallographic observation.

These alloys were examined using a scanning electron microscope (electrons source: tungsten filament, acceleration voltage: 20kV, imaging mode: back scattered electrons, magnifications: ×250 to ×1000, chemical analysis: energy dispersive spectrometry). Image analysis was carried out for quantitatively describing the chemical composition and high temperature exposures effects on microstructures. Vickers indentations with a 10kg load were performed to assess the effects on the ambient temperature hardness of the as-cast and aged alloys.

Per alloy again, a 5 mm × 5 mm × 2 mm parallelepiped was carefully prepared to carry out dilatometry tests up to 1250°C.

3. Results

Despite the high melting points of several of the elements to melt fusion was successful for all alloys. Obviously, no not-melted part was present in the ingot. Cutting was done without any difficulty, maybe a little harder for the cobalt-richest alloys than for the nickel-richest ones. The exposures to high temperature were achieved without over-oxidation of the samples (thanks to the presence of chromium in quantity high enough) and without partial melting of the alloys. The metallographic observations were of great interest and the dilatometry runs did not pose any problem. Results are reported as follows.

3.1. Control of the Chemical Compositions of the Obtained Alloys

The chemical compositions of the obtained alloys are displayed in Table-1. They were specified by EDS (average and standard deviation calculated from three ×250 full frame measurements). The contents in chromium are all the same, centered on 25.5 wt.%. The tantalum contents are all high enough to allow having Ta atomic content equal or slightly excessing the atomic carbon content. The carbon content cannot be directly measured because of its low atomic mass and its low content in the alloys. The Co content regularly increases from the "N alloy" (the cobalt-free Ni-based alloy) to the "C alloy" (the nickel-free Co-based alloy).

Table-1. Chemical composition of the alloys (three × 250 full frame EDS analyses); *: carbon content not possible to control by EDS, Its content is supposed to be well respected

Wt.%	N alloy	Nc alloy	Ncc alloy	Cnn alloy	Cn alloy	C alloy
Ni	Bal.	Bal.	Bal.	25.3±0.3	13.2±0.0	0
Co	0	13.2±0.2	25.7±0.4	Bal.	Bal.	Bal.
Cr	25.6±0.2	26.3±0.1	25.0±0.4	26.0±0.4	26.1±0.1	25.3±0.2
C	0.4*	0.4*	0.4*	0.4*	0.4*	0.4*
Ta	7.8±0.8	7.9±0.5	10.3±0.4	7.6±0.2	7.9±0.5	8.0±0.5

3.2. Microstructures of the Alloys: As–Cast Aged at 1200°C for 170 h Aged at 1250°C for 70h

The microstructures of the six alloys in the three different metallurgical states (as-cast, aged at 1200°C for 170 hours, and aged at 1250°C for 70 hours) are

Figure-1. Microstructures of the N alloy in the three states (as–cast, aged 170h at 1200°C, aged 70h at 1250°C)

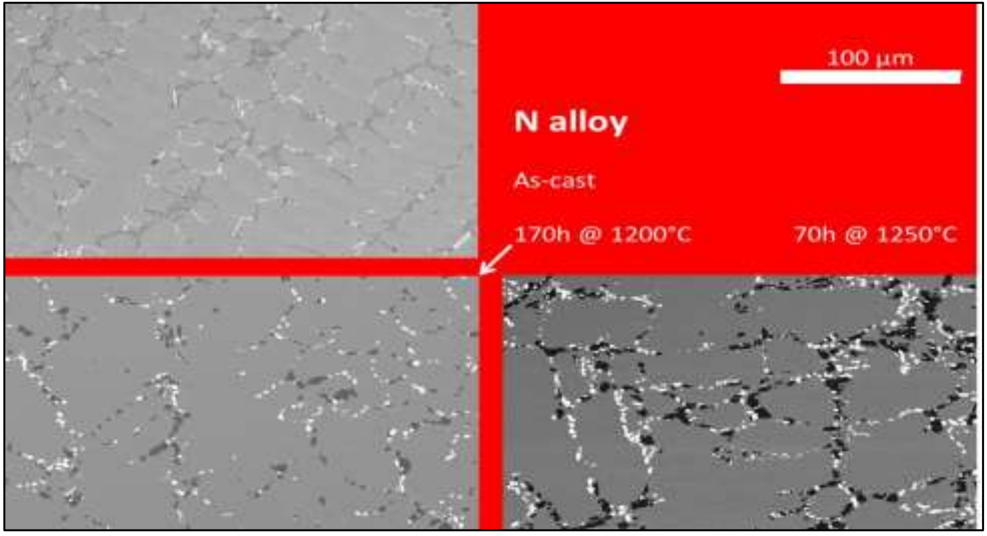


Figure-2. Microstructures of the Nc alloy in the three states (as–cast, aged 170h at 1200°C, aged 70h at 1250°C)

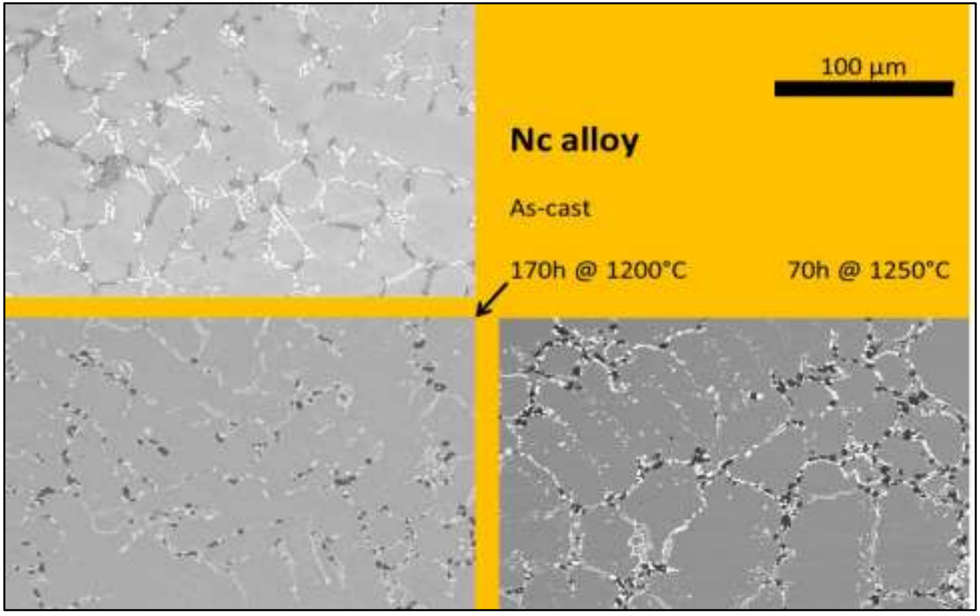


Figure-3. Microstructures of the Ncc alloy in the three states(as–cast, aged 170h at 1200°C, aged 70h at 1250°C)

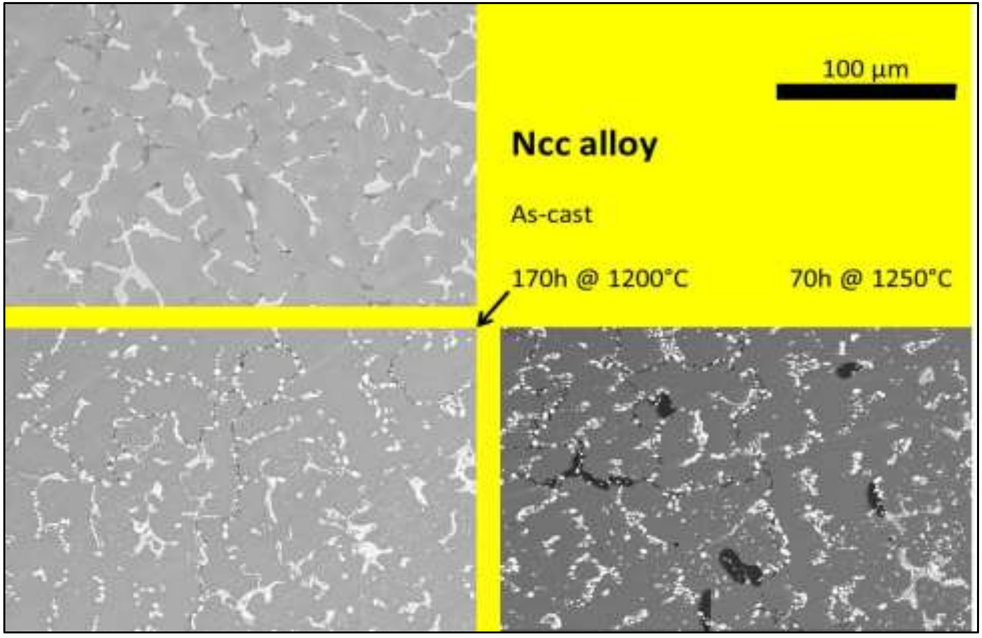


Figure-4. Microstructures of the Cnn alloy in the three states (as–cast, aged 170h at 1200°C, aged 70h at 1250°C)

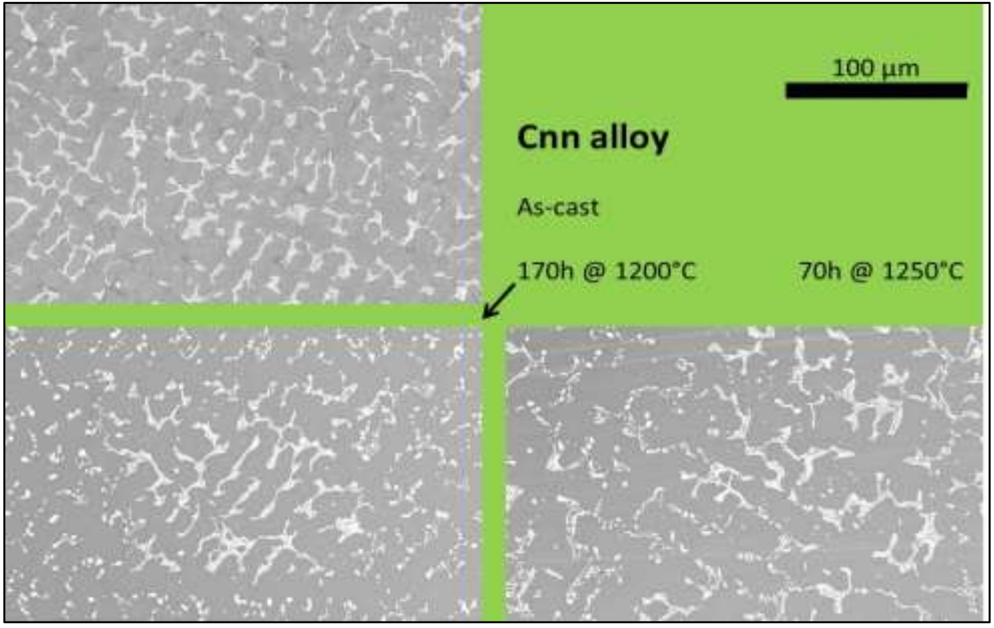


Figure-5. Microstructures of the Cn alloy in the three states (as–cast, aged 170h at 1200°C, aged 70h at 1250°C)

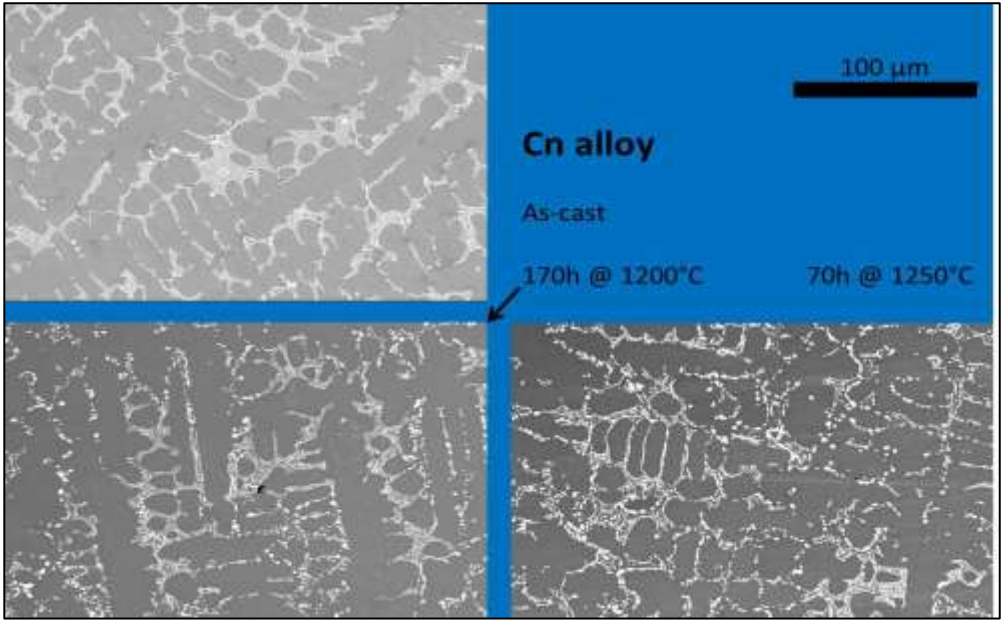
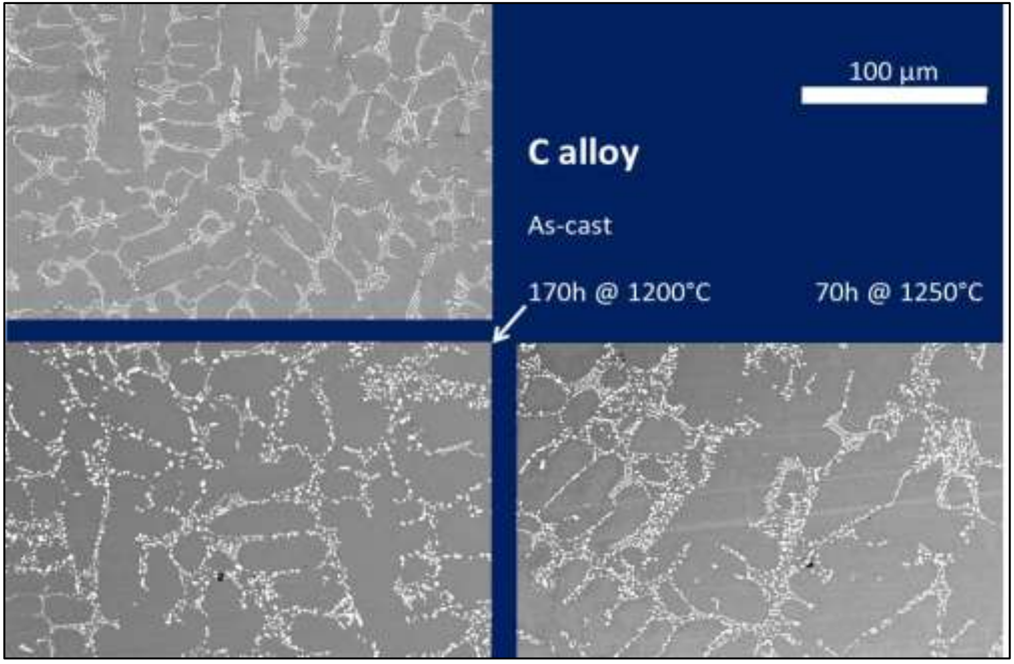


Figure-6. Microstructures of the C alloy in the three states(as–cast, aged 170h at 1200°C, aged 70h at 1250°C)



illustrated by ×500 SEM/BSE micrographs in Figure-1 ("N alloy"), Figure-2 ("Nc alloy"), Figure-3 ("Ncc alloy"), Figure-4 ("Cnn alloy"), Figure-5 ("Cn alloy") and Figure-6 ("C alloy").

All alloys initially own a dendritic structure and an interdendritic network of carbides (Figure-1 to Figure-6, top-left micrographs). The dendrites of solid solution matrix present scattered orientations, demonstrating the polycrystalline and equi–axed character of the alloys. The carbides are of two natures in the "N", "Nc" and "Ncc" alloys: deep dark carbides and white carbides. The first ones are chromium carbides, more precisely Cr_7C_3 carbides as identified by spot EDS analysis, while the second ones are TaC carbides. The Cr_7C_3 carbides present an acicular shape and are mixed with the peripherical parts of the dendrites. They are certainly eutectic carbides. The TaC carbides are script-like shaped and they are also mixed with matrix, forming another eutectic compound. When the cobalt content starts exceeding the nickel one, the chromium carbides almost wholly disappear. Indeed only rare and small dark carbides are present in the "Cnn" alloy, and do not exist anymore in the "Cn" and "C" alloys. At the same time the TaC carbides, single carbide phase to be still present, are much more present.

When these alloys are exposed to high temperature the initial morphology of the eutectic carbides has be replaced by another one: the chromium carbides and the tantalum carbides have lost their acicular shape and script-like shape, respectively. The two types of carbides are still present in the three nickel-richest alloys and the TaC carbides are still present in the three cobalt-richest ones, but all obviously get fragmented then coarsened. Seemingly, among the three nickel-richest alloys, neither the chromium carbides nor the tantalum carbides well resist to this morphological evolution. Furthermore a global microstructure coarsening (grain growth) seems having taken place, more for the "N" alloy (1250°C and 1200°C) than for the "Nc" alloy (only 1250°C), and for the "Nc" alloy more than for the "Ncc" alloy. In addition chromium carbides coalesced more at 1250°C than at 1200°C and more for the Ncc alloy than for the two other alloys. No such differences seem existing among the three cobalt–richest alloys: their TaC carbides are all fragmented but not specifically coarsened.

3.3. As-Cast and Aged Microstructures of Alloys: Quantitative Analysis

To more extensively specify the differences in microstructures between the six alloys and between the three states (as–cast, aged at 1200°C and aged at 1250°C) surface fractions measurements were carried out using the image analysis tool of the Adobe Photoshop CS software. After grey level rating the surface fractions of the dark carbides and of the white carbides were measured on three randomly taken BSE ×1000 micrographs. The obtained average and standard deviation values are given in Table-2 for the dark chromium carbides and in Table-3 for the white TaC carbides. One can see first that when nickel is progressively replaced by cobalt as base element, the surface fraction of Cr_7C_3 in the as-cast microstructure rapidly decreases from the “N alloy” (3 surf.%) to the “Cnn” one (0 surf.%) and do not exist anymore in two last alloys very rich in cobalt. At the same time the TaC surface fraction increases from slightly more than 2 surf.% for stabilizing at almost 8 surf.% for the three cobalt-richest alloys. The 170h–exposure at 1200°C induces a slight decrease in surface fraction for the chromium carbides in the three nickel–richest alloys. The opposite effect is curiously observed after the 70h–exposure at 1250°C: the chromium carbide surface fractions are even significantly higher than in the as–cast condition. A similar effect of the high temperature exposure is noted for the tantalum carbides for the nickel-richest alloys again. In the case of the three cobalt–richest alloys, no so significant change in carbide surface fraction can be noted.

Table-2. Surface fractions in the chromium carbides (from three × 1000 BSE images)

Surf.%	N alloy	Nc alloy	Ncc alloy	Cnn alloy	Cn alloy	C alloy
As-cast	3.10±0.28	2.44±0.24	1.74±0.43	0.06±0.03	0.02±0.02	0.02±0.01
170h 1200°C	3.06±0.29	2.63±1.24	0.37±0.28	0.03±0.03	0.01±0.01	0.02±0.02
70h 1250°	4.98±0.73	2.96±0.61	4.36±1.17	0.13±0.11	0.01±0.01	0.06±0.02

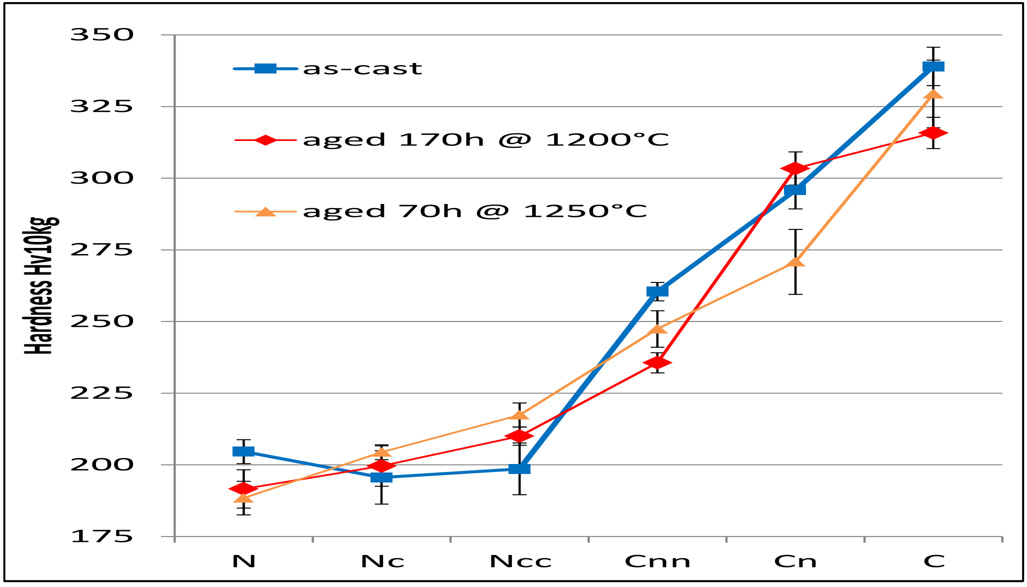
Table-3. Surface fractions in the chromium carbides (from three × 1000 BSE images)

Surf.%	N alloy	Nc alloy	Ncc alloy	Cnn alloy	Cn alloy	C alloy
As-cast	2.26±0.47	4.18±0.47	6.13±0.84	7.73±0.79	9.42±1.39	7.99±0.36
170h 1200°C	1.91±0.16	5.55±1.71	7.46±0.89	9.68±1.89	7.65±1.27	6.64±0.34
70h 1250°	2.92±0.96	7.10±0.29	9.06±1.21	7.58±0.79	8.51±4.18	7.54±0.59

3.4. Hardness

The cobalt/nickel balances and the changes in carbides morphology and surface fractions may have consequences on the hardness of the alloys. Five indentations were carried out per sample according to the Vickers method under a 10kg load. The obtained results are presented in the graph shown in Figure-7. Obviously, this is much more the Co/Ni ratio than the metallurgical state of the alloy which governs the hardness. When Co, initially absent, progressively replaces Ni, the global hardness increases from about 200 to about 325 Hv_{10kg}. More precisely, this is only with the third Co addition (from the “Cnn” alloy), the one which makes cobalt becoming the base element, that hardness takes off. Concerning the effects of the high temperature aging treatments, their effects are not clear: tendency to hardening for the Ni–richest alloys and of softening for the Co–richest alloys.

Figure-7. Hardness of all alloys for the three states (as-cast, aged 170h at 1200°C, aged 70h at 1250°C)



3.5. Thermal Expansion

The as-cast alloys cut as parallelepipeds were subjected to dilatometry in order to explore their behaviors in thermal expansion. The obtained dilatometry curves, as illustrated by the examples given in Figure-8 ("N" alloy) and Figure-9 ("C" alloy), are rather regular and present a slight upward curvature. There are no evident differences among the six curves and the average thermal expansion coefficient over the [25–1250°C] temperature range do not vary significantly passing from one alloy to another, as shown in Figure-10. All values are concentrated around 20×10^{-10} $°C^{-1}$. In addition, despite the very high temperature of test end (1250°C), no inversion, and even no slow–down, of expansion was noted when arriving in the neighborhood of the maximal temperature, in contrast with what was earlier encountered for simpliest nickel–based, cobaltvbased and iron-based alloys (Berthod, 2008).

Figure-8. Thermal expansion behavior of the studied alloys (here the N alloy)

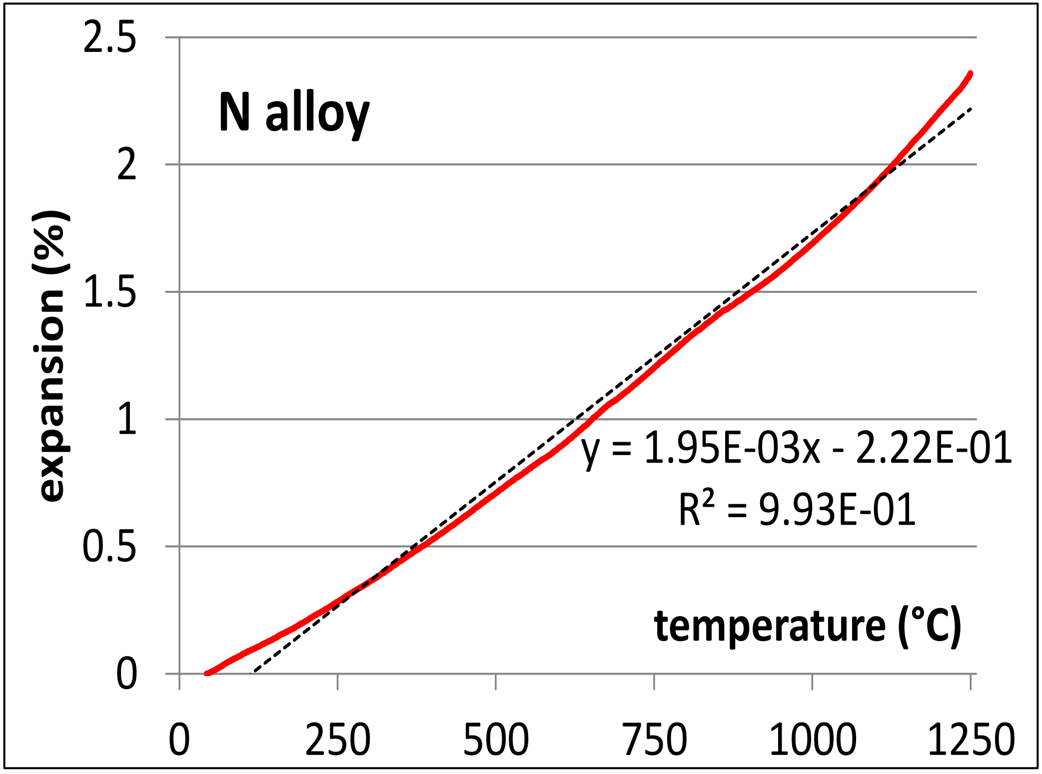


Figure-9. Thermal expansion behavior of the studied alloys (here the C alloy)

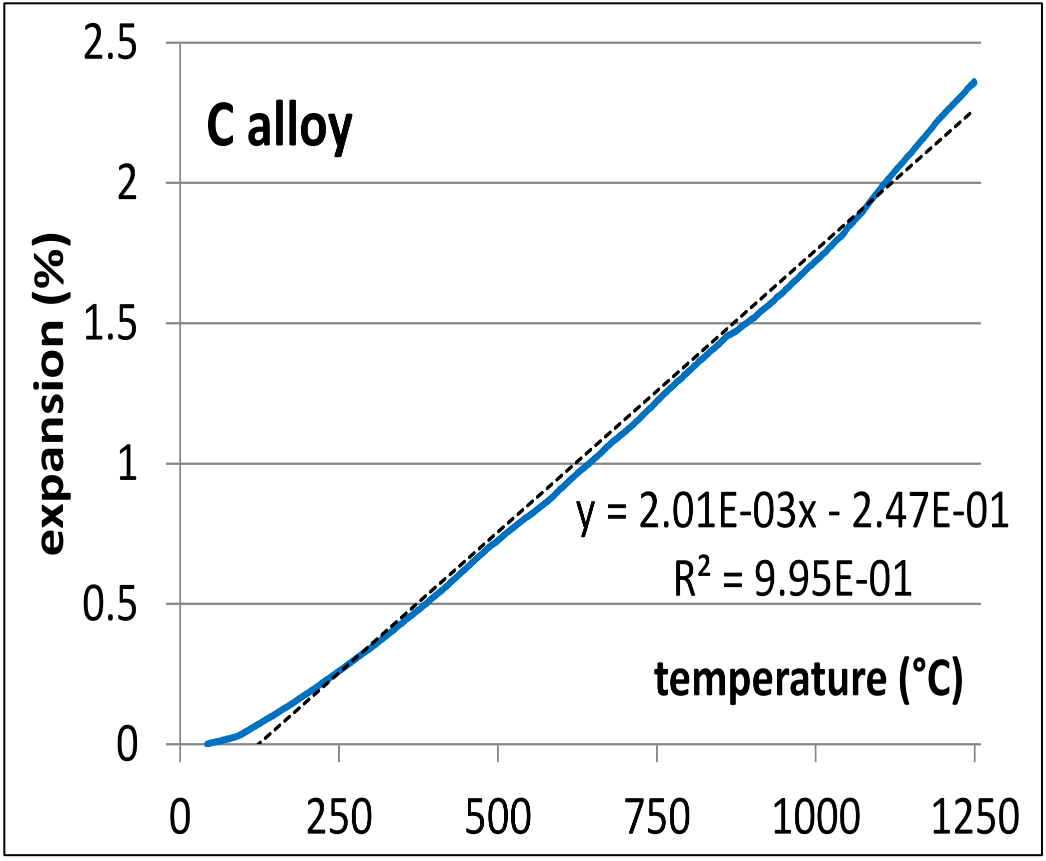
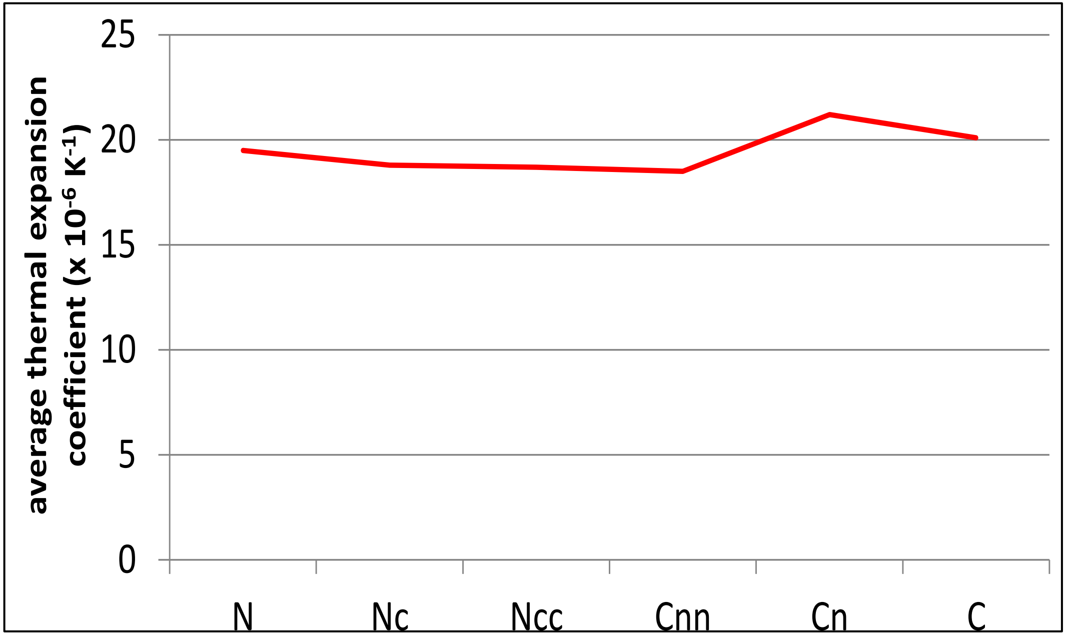


Figure-10. The average thermal expansion coefficients for all alloys



4. Discussion

The first observation which was done above concerns the matrixes and the natures of the obtained population of carbides. The dendritic morphology of the matrix suggests that solidification was systematically influenced by a constitution undercooling which promoted instabilities of the solid/liquid interface. This also indicated that the cobalt-based or the nickel-based solid solution was the first solid phase to nucleate and to grow. All carbides are concentrated in the interdendritic spaces where the last liquid – enriched in carbon, chromium and tantalum – to solidify according to eutectic reactions, and disappear by becoming a mix of matrix and carbides. Two distinct eutectics were observed in the nickel–richest alloys: matrix + Cr_7C_3 carbides and matrix + TaC carbides, but no ternary eutectic combining matrix and the two types of carbides. The cobalt–richest alloys were simplier: double-phased matix + TaC. Taking into account the rather fast cooling in liquid state and in solid state as well as the rather fast solidification (small ingots in contact with a cold copper crucible), the different phase transformations were necessarily realized out of thermodynamic equilibrium. This is thus not surprising that the aging of the alloys at high temperature and during rather long times have changed the alloys' structures, notably the fractions in chromium carbides and/or in tantalum carbides. The microstructures were chemically homogeneized, this erasing the chemical segregations having taken place during solidification notably, and the favorably high and long temperatures and durations of the exposures have allowed the alloys converging to their thermodynamically stable states. The chemical homogenization and thermodynamic stabilization were accompanied by a change in morphology for the carbides. These morphological changes of the carbides, from elongated shapes (acicular or script-like) to much blockier or rouner shapes, powered by the minimization of the interfacial energies, were more or less advanced depending of the type of carbides and the type of matrix. This is well understandable when one consider the difference of high temperature stability between the chromium carbides (the least stable ones) and the tantalum carbides (the most stable), the diffusion easiness (Cr is a smaller atom than Ta, Cr and Ta diffuse less easily in a cobalt matrix than in a nickel matrix), and maybe of the carbide–matrix interfacial energy which may depend on both the matrix's nature and the carbide phase's nature.

Concerning the properties, only two ones were considered here: the hardness at ambient temperature and the thermal expansion behavior. The hardness was much more dependent on the base element than on the carbides (nature and morphology). No difference was noticeable concerning thermal expansion (globally the same dilatation curves and the same average TEC for all alloys), except a difference with alloys earlier studied: here no slow–down or inversion were seen on the end of the dilatometry curves despite the high level of temperature reached. Obviously, the carbides were here not in quantity high enough to obstruct the matrix expansion, in contrast with what occurred with alloys richer in carbon.

5. Conclusion

The six alloys studied here, representative of the Ni–Co–Cr–C–Ta quinary system, are either double–phased or triple–phased and combine a principal metallic volume with dispersed ceramic precipitates. These later ones, of a nature mainly selected by the choice of the base element, can be shaped using solidification process as well as by exposing them to heat. For the properties under interest in this work, hardness and thermal expansion, the dimensional and morphological characteristics of the secondary phases were without significant effect. Further investigations may concern the high temperature mechanical behavior, notably creep deformation, for which these particles will surely play a much important role.

References

[1] Bradley, E. F., 1988. *Superalloys: A technical guide*. Metals Park: ASM International.

[2] Donachie, M. J. and Donachie, S. J., 2002. *Superalloys: A technical guide*. 2nd ed. Materials Park: ASM International.

[3] Youdelis, W. V. and Kwon, O., 1983. "Carbide phases in nickel-base superalloy: nucleation properties of MC type carbide." *Metal Science,* vol. 17, pp. 385–388.

[4] Qin, X. Z., 2008. "Decomposition of primary MC carbide and its effects on the fracture behaviors of a cast Ni-base superalloy. Materials Science and Engineering, A: Structural Materials: Properties." *Microstructure and Processing,* vol. A485, pp. 74–79.

[5] Li, X. W., 2014. "Effect of solidification condition and carbon content on the morphology of MC carbide in directionally solidified nickel-base superalloys." *Journal of Materials Science and Technology,* vol. 30, pp. 1296–1300.

[6] Eng, R. D. C. and Donachie, M. J., 1972. "Microstructure of WI-52 cast cobalt-base high-temperature alloy." *Journal of the Institute of Metals,* vol. 100, pp. 120–124.

[7] Felten, E. J. and Gregg, R. A., 1964. "The physical metallurgy and oxidation characteristics of a cobalt-base superalloy, SM-302." *ASM Transactions Quarterly,* vol. 57, pp. 804–822.

[8] Wei, Z. W., 2015. "Microstructure Evolution of K6509 Cobalt-base Superalloy for Over-temperature." *Procedia Engineering,* vol. 99, pp. 1302–1310.

[9] Vandermousen, R. F., 1976. "Directional solidification of cobalt-base superalloys." *Cobalt,* vol. 1, pp. 6–12.

[10] Kofstad, P., 1988. *High temperature corrosion*. London: Elsevier applied science.

[11] Young, D. J., 2008. *High temperature oxidation and corrosion of metals*. Amsterdam: Elsevier corrosion series.

[12] Michon, S., 2003. "Application of thermodynamic calculations to study high temperature behavior of TaC-strengthened Co-base superalloys." *Calphad,* vol. 27, pp. 289–294.

[13] Berthod, P., 2004. "Experimental and thermodynamic study of the high temperature microstructure of tantalum containing nickel-based alloys." *Calphad,* vol. 28, pp. 159–166.