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Stable Microstructural States at 1200°C of Ni–Based Alloys Containing Chromium Carbides and Tantalum Carbides

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Abstract Nickel–based superalloys are among the strongest and corrosion–resistant metallic materials for uses at high temperature. For some of them, chromium plays a double role, on each the two previous properties. The purpose of this study is exploring how cobalt additions may influence the balance of two types of carbides which may be present simultaneously in the microstructure: chromium carbides and tantalum carbides. Three alloys were elaborated: a cobalt–free reference one and two versions of this reference alloy with two additions of cobalt. The microstructures obtained after solidification were considered with interest, but what these microstructures became after long exposure at high temperature was particularly studied. Cobalt demonstrated a significant effect on the microstructure, as–cast or 1200°C–aged. Adding cobalt induces a shift from equivalent populations of chromium carbides and tantalum carbides toward predominance of the tantalum carbides (TaC). After about a week of exposure to 1200°C the carbide network was more or less affected but the TaC showed better resistance against the morphological transformations known to be detrimental for the mechanical properties at high temperature. Beside morphology, the fractions of strengthening particles are generally a key factor for the mechanical sustainability of superalloys. The volume fractions of TaC in the three alloys were therefore estimated following two ways: deduction from the Ta content in matrix and thermodynamic calculations. Clearly, the presence of cobalt and high amount of this element promote high level of TaC volume fraction for given Ta and C contents in alloy.

Keywords High temperature alloys; Nickel alloys; Cobalt; tantalum carbides; Thermodynamic modeling

1. Introduction

Pieces and components working at temperatures as high as 1000°C and above may have an elongated shape or a more compact one. In the first case, with as emblematic example: turbine blades, directionally solidified (DS), single crystalline (SX) or oxide dispersion strengthened (ODS) alloys may be used [1]. Beside, more compact components cannot take benefit of the preceding excellent superalloys and of their very favorable microstructures. They must be fabricated by powder metallurgy, additive manufacturing, forging or conventional casting [2]. The superalloys elaborated following these other fabrication ways are necessarily polycrystalline and their grain boundaries (GB) are randomly oriented. Taking into account the mechanical weakness of GB at high temperatures the presence of hard particles must be present in the interdendritic spaces. Carbides are among the earliest strengthening hard particles which were used in polycrystalline superalloys [3]. The first carbides to be employed to strengthen superalloys were chromium carbides and chromium & tungsten carbides, which involved a part of the rather high chromium quantity added to allow the alloys resisting both hot oxidation by gases and hot corrosion by molten deposits[4,5]. Later, with

the increase in operating temperatures carbides more refractory carbides appeared in the microstructures, beside chromium carbides [6,7]. Monocarbides, i.e. of the MC stoichiometry, are among the best ones in term of strengthening efficiency and of high temperature thermodynamic stability. They can be of various types [8]. The most common ones are certainly tantalum monocarbides which may lead to unexpected mechanical properties at very high temperatures [9]. This is also the case of hafnium monocarbides [10]. Other M elements are also able to form MC carbides but the more interesting in term of cost and of hot oxidation resistance remains TaC. Tantalum monocarbides are easy to obtain as single carbide phase in cobalt-based alloys [11, 12] but this is more problematic in nickel-based alloys [13]. Unfortunately this is sometimes a nickel-based alloy that is preferred to a cobalt-based one, for various possible reasons (machinability, oxidation behavior, cost). By adding not too high amounts of cobalt in a nickel-based superalloys designed to be TaC-reinforced it is possible to rate the tantalum carbides / chromium carbides ratio at higher values for better compromise between mechanical properties, chemical resistance and fabrication cost.

In this work, two Co additions in a nickel-based alloy designed to be possibly reinforced by TaC carbides only, were envisaged. Three alloys were elaborated and exposed to high temperature. Their microstructures existing just after fabrication by foundry and after a long isothermal exposure in a high temperature furnace were characterized. The volume fractions of the TaC carbides were studied versus the Co addition.

Materials and Methods

The chemical compositions wished for the three alloys were Ni(bal.)–25Cr–0.4C–6Ta (“Nicalloy”), Ni(bal.)–13.7Co–25Cr–0.4C–6Ta (“Nic2”) and Ni(bal.)–27.4Co–25Cr–0.4C–6Ta (“Nic3”). All these targeted contents are in weight percent. They were elaborated from small parts of pure elements, using a high frequency induction furnace (CELES, France) under controlled atmosphere (300mbars of pure Argon, AIR LIQUIDE, France). Small ingots (mass: about 40 grams) were obtained and cut using metallographic precision saw to obtain parts for initial microstructure and chemical composition control, and for high temperature exposure.

The parts to be exposed at high temperature were placed in alumina nacelles, in the hottest zone of a resistive muffle furnace (NABERTHERM, Germany). They were heated to reach 1200°C, the temperature at which they were constantly maintained during a week.

The as-cast part and the aged part of each alloy were embedded in metallographic resin (ESCIL, France), ground/polished with SiC papers/alumina-enriched textile, and characterized by Back Scattered Electron (BSE) imaging and Energy Dispersion Spectrometry (EDS) composition control, with a Scanning Electrons Microscope from JEOL (Japan, model: JSM-6010LA).

In parallel the theoretic stable states at high temperature of the three alloys and of the quaternary/quinary systems to which they belong, were explored using the Thermo-Calc software (Version N) and the database especially prepared from the SSOL commercial one. The descriptions of the following subsystems were added to SSOL to allow it treating the cases of tantalum-containing alloys:

- the binary systems Ni-Ta, Co-Ta and Cr-Ta [14–16],
- and the ternary systems Cr-Ni-Ta, Ni-Ta-C and Ta-Co-C [17–19].

Results and Discussion

Chemical Composition and Microstructures

The values of weight contents in Co, Cr and Ta as controlled by EDS are displayed in Table 1.



Table 1: Compositions of the elaborated alloys (5 full frame $\times 250$ EDS analyses \rightarrow average value \pm standard deviation value)

All contents in wt.%	Nic1	Nic2	Nic3
Ni	Balance		
Co	/	13.4 \pm 0.2	26.9 \pm 0.2
Cr	25.7 \pm 0.2	26.2 \pm 0.2	25.6 \pm 0.2
Ta	6.9 \pm 0.3	7.0 \pm 0.3	7.1 \pm 0.3
C	Supposed to be 0.4 (well respected)		

The Co and Cr contents which were targeted can be considered as successfully obtained. The Ta contents are a little too high by comparison to the wished values. The C content cannot be controlled by EDS over the whole alloy, in contrast with the C content in C-rich particles (as carbides) for which spot analyses can be accurate.

The wished C content can be considered as being itself successfully obtained by looking to the carbides populations: the as-cast microstructures and the 1200°C-aged ones. These ones are illustrated by SEM/BSE micrographs in Figure 1.

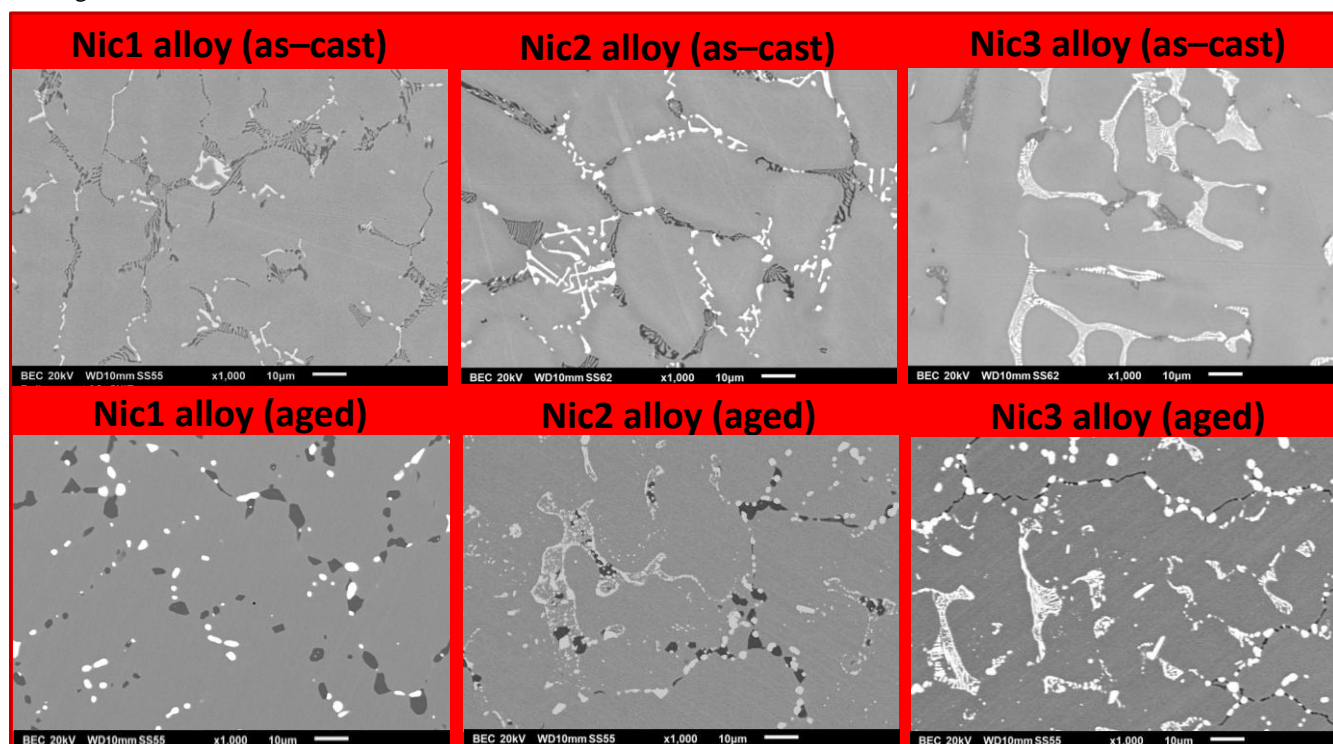


Figure 1: As-cast (top) and 1200°C-aged (bottom) microstructures of the three alloys (SEM/BSE micrographs)

By considering first the microstructures of the as-cast alloys (top micrographs) one can see that the three alloys have a dendritic matrix probably the first solid phase to crystallize at the beginning of solidification, since all the other particles are located between dendrites. These particles were identified by EDS spot analysis. The high concentrations of the black particles in carbon and in chromium suggest that these are chromium carbides. Furthermore, since the Cr/C atomic ratio is closer to 2 than to 4, these chromium carbides are of the Cr₇C₃ stoichiometry. EDS also allowed identifying the white particles: the predominance of both C and Ta in EDS spot analysis results and the atomic contents in tantalum and carbon which are close to one another, allow claiming that they are TaC monocarbides.

The dendritic structure of the matrix and the fact that all the other present compounds should be interdendritically located are confirmed by the isopleth section calculated by Thermo-Calc and presented in Figure 2. However, some discrepancies appear concerning the natures of carbides: according to thermodynamic calculations TaC carbides should appear during solidification only for the third alloy ("Nic3", the Co-richest one).

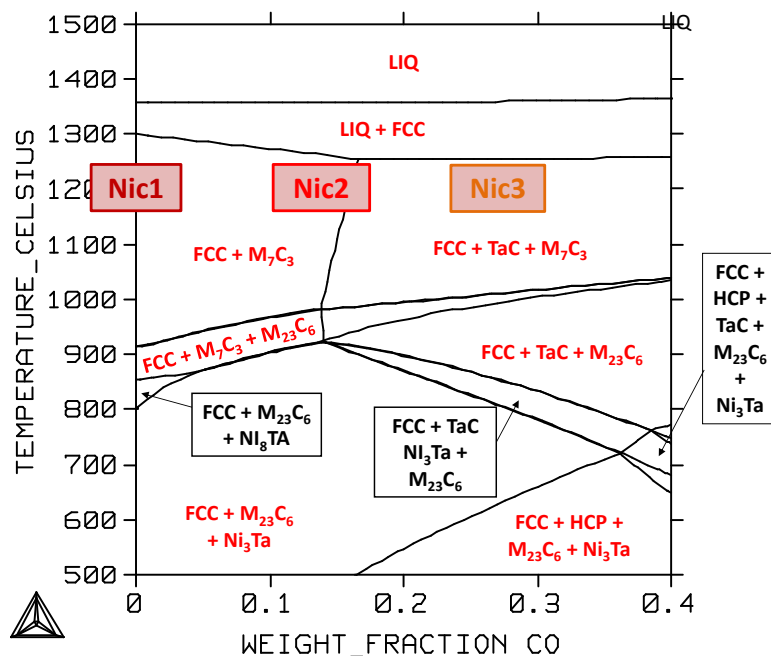


Figure 2: Isopleth section at {25 wt.%Cr, 0.4wt.%C and 6 wt.%Ta} of the {Ni, Co, Cr, C, Ta} system, calculated with Thermo-Calc; position of the 3 alloys when they were at 1200°C

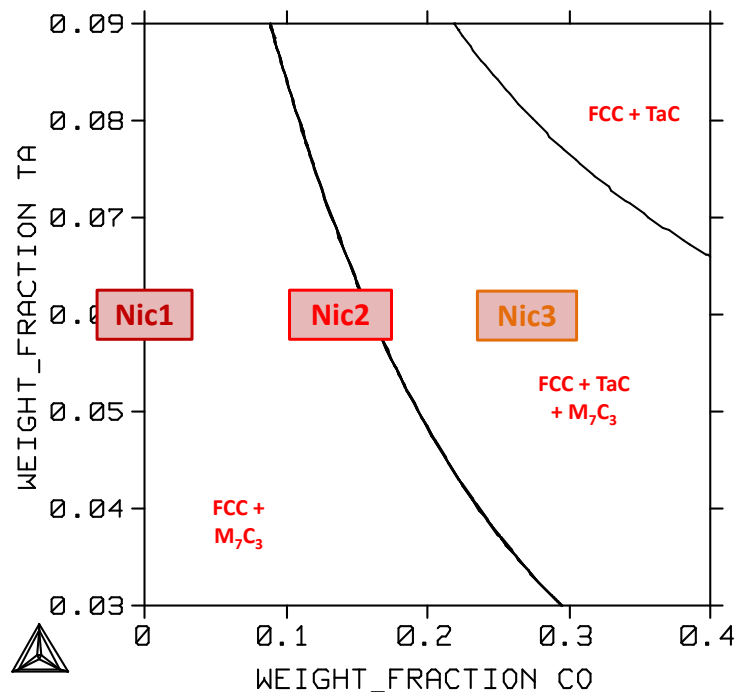


Figure 3: 1200°C-section at {25 wt.%Cr and 0.4wt.%C} of the {Ni, Co, Cr, C, Ta} system with varying contents in Ni(Co) and Ta, calculated with Thermo-Calc; positions of the 3 alloys



Figure 3 allows better seeing the theoretic constitution of the alloys at 1200°C. After a week spent at this temperature all the alloys can be considered as thermodynamically stabilized (the post-isothermal cooling was not slow enough to allow significant changes). This 1200°C–isothermal section confirms that the “Nic1” and “Nic2” alloys can be expected as being TaC–free. In contrast the position of the “Nic3” alloy on the middle–line in the triple–phased domain (FCC + M₇C₃ + TaC) is in good agreement with the triple–phased state of this alloy after aging, but also suggests that M₇C₃ and TaC should be present in similar quantities: this is not the case since the “Nic3” alloy contains much more TaC than M₇C₃(which can be considered almost as traces...).

Quantification of the TaC carbides fractions

For a given weight content in carbon the C atoms must be principally involved in the constitutions of carbides in presence of rather high contents in two strong carbides–former elements: 25 wt.%Cr and 6 wt.%Ta. Carbon is necessarily also present in interstitial solution in matrix – for thermodynamic reasons: equilibrium means equal chemical activity in all phases – but in quantity low enough to be neglected. Focus was done on the TaC carbides since their presence induces significant relative decrease in Ta content in the matrix. This allows specifying more accurately the mass fraction of TaC carbides than the more limited relative decrease in matrix chromium content induced by the Cr₇C₃ presence. By assuming that the mass fraction of chromium carbides is low enough to allow considering that: 1/its sum with the matrix mass fraction is very close to the mass fraction of matrix alone, and 2/the average Ta content in the double–phased {matrix + Cr₇C₃} domain is very close to the Ta content in the matrix alone. With these hypotheses one can use the following equations to exploit the Ta contents in matrix at 1200°C to deduce the TaC mass fractions:

$$F_{\text{TaC}}^{\text{mass}} = \{M_{\text{TaC}} \times (\text{WC}_{\text{Ta}}^{\text{ALL}} - \text{WC}_{\text{Ta}}^{\text{MAT}})\} / \{M_{\text{Ta}} - M_{\text{TaC}} \times \text{WC}_{\text{Ta}}^{\text{MAT}}\} \quad (\text{eq.1})$$

$$F_{\text{TaC}}^{\text{vol}} = \{F_{\text{TaC}}^{\text{mass}} / \text{VM}_{\text{TaC}}\} / \{(1 - F_{\text{TaC}}^{\text{mass}}) / \text{VM}_{\text{mat}} + F_{\text{TaC}}^{\text{mass}} / \text{VM}_{\text{TaC}}\} \quad (\text{eq. 2})$$

In these equations, $F_{\text{TaC}}^{\text{mass}}$ is the mass fraction of TaC, M_{TaC} is the molar mass of TaC (193 g/mol), $\text{WC}_{\text{Ta}}^{\text{ALL}}$ is the Ta weight content in the whole alloy (6 wt.%), $\text{WC}_{\text{Ta}}^{\text{MAT}}$ is the Ta weight content in the matrix (determined by EDS), M_{Ta} is the molar mass of tantalum (181 g/mol), $F_{\text{TaC}}^{\text{vol}}$ is the volume fraction of TaC, VM_{TaC} is the volume mass of the TaC carbide (14.3 g/cm³) and VM_{mat} is the volume mass of the matrix (estimated at 9 g/cm³).

The chemical compositions of the matrixes of the three alloys in their 1200°C–states are given in Table 2, together with the Co, Cr, Ta and C contents issued from thermodynamic calculations. The real Cr contents in the matrixes as specified by EDS spot analysis are logically higher than predictions since chromium carbides are present in lower quantity than predicted. For the inverse reasons, the real Ta contents in matrix are lower than predicted (more TaC in real alloys than according to calculations).

Table 2: Composition of the matrixes of the 1200°C–aged alloys (1 : calculated; 2: EDS–measured chemical compositions of the matrix, average ± standard deviation from 5 full frame ×250 analyses)

MATRIX at 1200°C (wt.%)	Nic1	Nic2	Nic3
Co (Th-C)	/	14.20	28.77
Co (EDS)	/	14.1 ±0.2	28.4 ±0.4
Cr (Th-C)	22.38	22.47	24.79
Cr (EDS)	24.3 ±0.2	26.1 ±0.2	26.8 ±0.2
Ta (Th-C)	6.25	6.25	3.17
Ta (EDS)	4.3 ±0.2	2.9 ±0.2	1.9 ±0.2
C (Th-C)	0.05	0.05	0.06

The Ta contents in matrix were exploited to estimate the mass fractions of TaC carbides according to equation (1), and thereafter their mass fractions according to equation (2). The corresponding values are presented in Table 3, together with the mass fractions resulting from the thermodynamic calculations and the volume fractions after conversion according to equation (2) too. Mass or volume fractions of TaC coming from experiments are logically higher than the ones coming from calculations, taking into account the previous qualitative observations.



Table 3: TaC volume fractions issued from Thermo–Calc calculations, and TaC volume fractions deduced from the EDS–measured Ta contents in the matrixes of the 1200°C–aged alloys (1: average Ta in matrix - sd, 2: average Ta in matrix, 3: average Ta in matrix + sd; sd: standard deviation)

MATRIX at 1200°C (wt.%)	Nic1	Nic2	Nic3
Thermo-Calc (deduced from this mass.%)	0 (0)	0 (0)	2.00 (3.20)
1200°C– aged vol.% TaC from wt.%Ta in matrix (EDS)	1.34 ⁽¹⁾ 1.20 ⁽²⁾ 1.06 ⁽³⁾	2.31 ⁽¹⁾ 2.17 ⁽²⁾ 2.04 ⁽³⁾	2.99 ⁽¹⁾ 2.86 ⁽²⁾ 2.72 ⁽³⁾

The average values of TaC volume fraction provided by the treatment of the Ta weight contents in matrix were checked by digitalizing SEM/BSE pictures. The digitalized pictures were then rated – using the image analysis tool of the Adobe Phoshop CS software – to find the grey level threshold which allows obtaining the surface fraction of the same value as (or at least the closest values to) the average volume fractions displayed in the last line of Table 3. The corresponding digitalized pictures, made of black pixels and white pixels only, were thereafter visualized to be compared to the initial pictures still in grey levels.

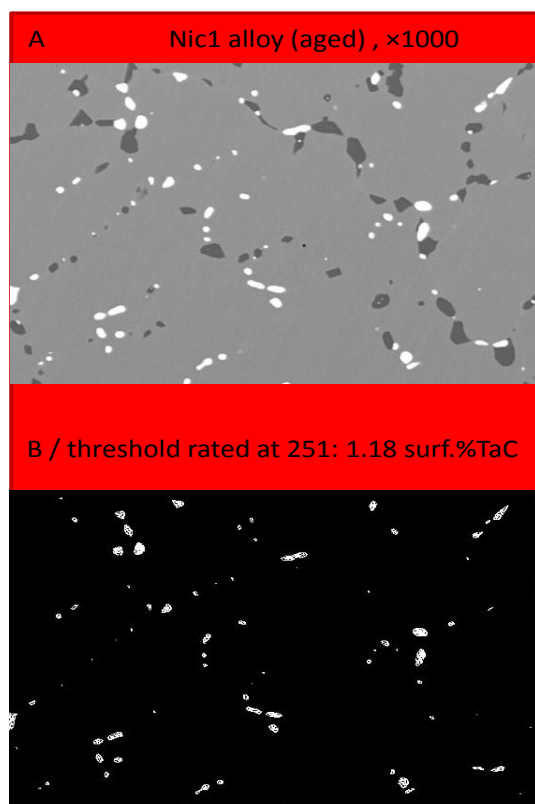


Figure 4: 1200°C–aged “Nic1” alloy; A: initial SEM/BSE micrograph, and B: its digitalized version (1.18 surf.%TaC for threshold = 251 over 255)

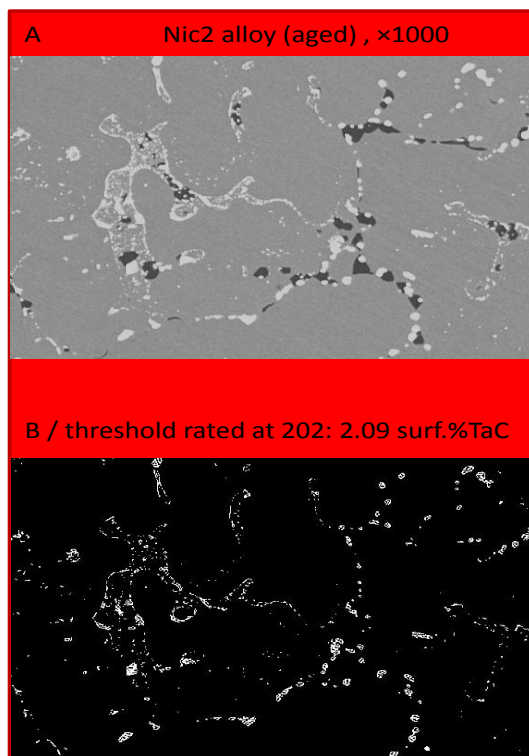


Figure 5: 1200°C-aged “Nic2” alloy; A: initial SEM/BSE micrograph, and B: its digitalized version (2.09 surf.%TaC for threshold = 202 over 255)

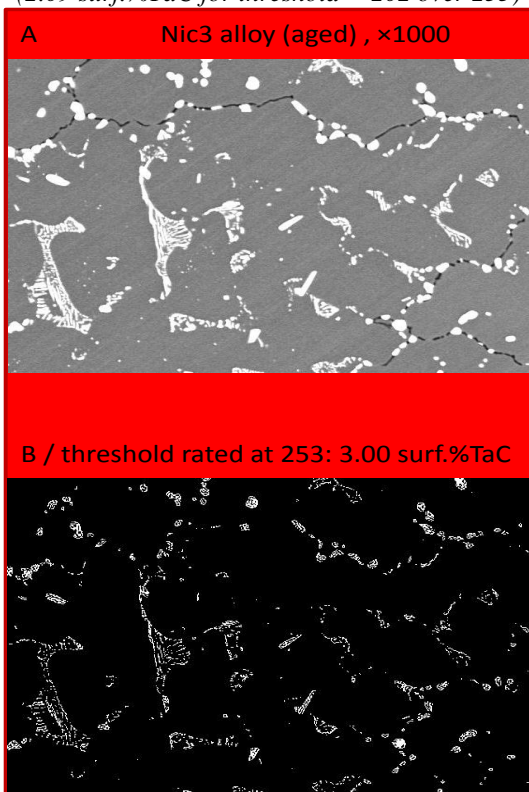


Figure 6: 1200°C-aged “Nic3” alloy; A: initial SEM/BSE micrograph, and B: its digitalized version (3.00 surf.%TaC for threshold = 253 over 255)

The results, illustrated in Figure 4, Figure 5 and Figure 6, for the “Nic1”, “Nic2” and “Nic3” alloys respectively, suggest that the obtained fractions obtained using the Ta weight content in matrix are realistic, since the two pictures, the first one in grey levels and the second in black and white, are similar in each case; the TaC carbides of the first pictures (initial SEM/BSE micrograph) and its digitalized version both give the same representation of the TaC carbides.

Exploring theoretic microstructures for wider Ta, Cr and C variations

Thermodynamic calculations successfully found data concerning the sequences of solidification and the beneficial effect of cobalt additions on the presence and amount of tantalum carbides. However, some qualitative disagreements appeared concerning the carbides population in the “Nic1” and “Nic2” alloys at 1200°C. For the “Nic3” alloy the disagreement was not qualitative but only quantitative. This is clear that the database must be incomplete. Some subsystems including tantalum were added but all the subsystems with tantalum are not present. Many of them are still lacking and this is certainly the reason of the mismatches between real alloys and thermodynamic calculations which were seen here. This does not forbid to use – with caution – the present thermodynamic calculation tool to explore the microstructural change tendencies possibly induced by more extended content increases for such-and-such elements. Three examples are given in Figure 7–9 concerning wider variations in Ta (Figure 7), Cr (Figure 8) and C (Figure 9), for alloys in which Ni is more or less substituted by cobalt. Especially concerning the TaC / Cr₇C₃ balance, these three isothermal sections clearly show that Co and Ta favor tantalum carbides at the expense of chromium carbides while Cr and C inversely favor the additional presence of chromium carbides.

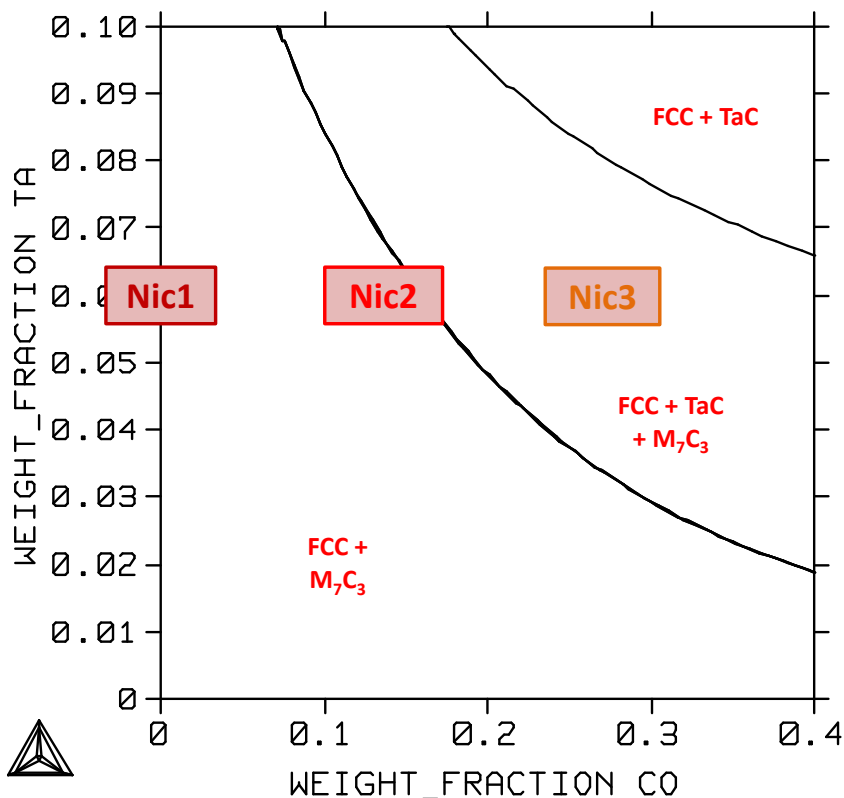


Figure 7: 1200°C–isothermal section at {6 wt.%Ta and 0.4wt.%C} of the {Ni, Co, Cr, C, Ta} system with varying contents in Co(Ni) and Ta (0–10 wt.%) calculated with Thermo–Calc with the positions of the 3 alloys



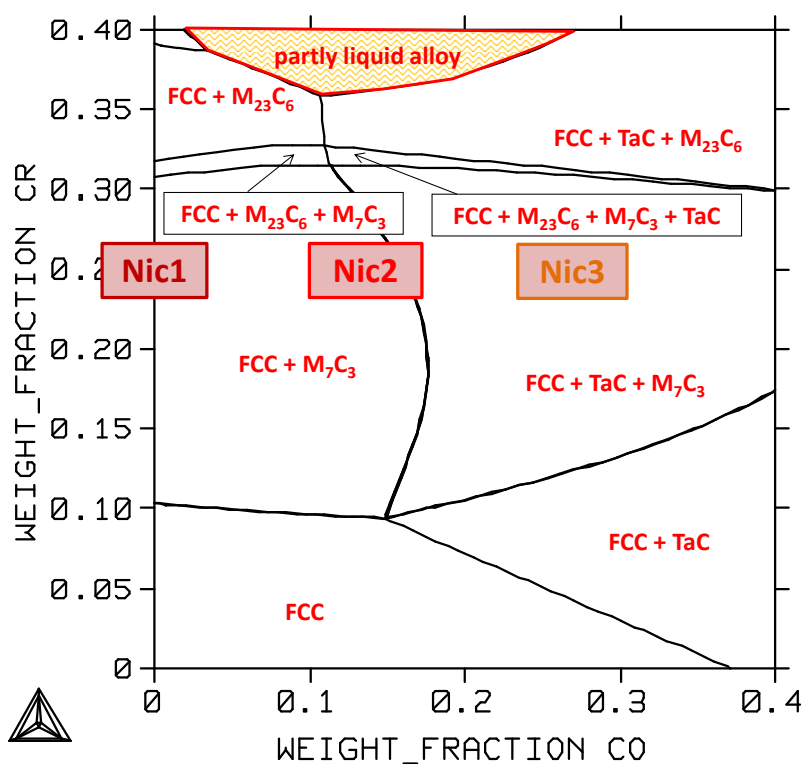


Figure 8: 1200°C–isothermal section at {25 wt.%Cr and 0.4wt.%C} of the {Ni, Co, Cr, C, Ta} system with varying contents in Co(Ni) and Cr (0–40 wt.%) calculated with Thermo–Calc with the positions of the 3 alloys

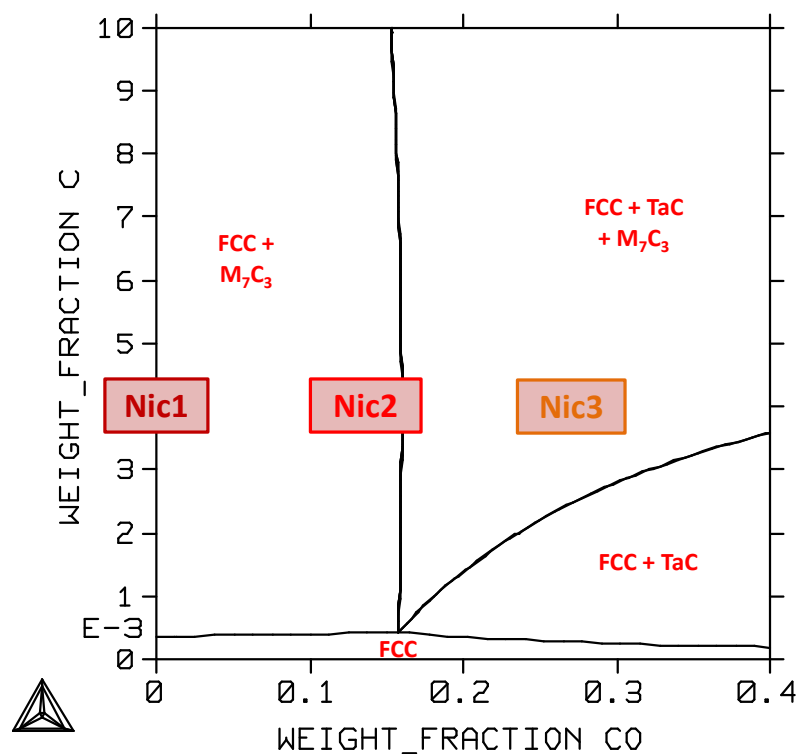


Figure 9: 1200°C–isothermal section at {25 wt.%Cr and 6 wt.%Ta} of the {Ni, Co, Cr, C, Ta} system with varying contents in Co(Ni) and C (0–1 wt.%) calculated with Thermo–Calc with the positions of the 3 alloys

Conclusion/Outlooks

In total absence of cobalt, for 25wt.%Cr, 0.4wt.%C and 6wt.%Ta, there are as many chromium carbides as tantalum carbides. The carbon is almost fairly distributed between the two types of carbides. Experimentally adding more and more cobalt unbalances this distribution in favor of tantalum carbides, and this may be beneficial to the high temperature strength of the alloy by having more highly stable carbides (and also stronger matrix, solid solution hardened by Co). Nothing was experimentally done in this work concerning the effect of chromium but one can imagine that a decrease in chromium content may be deleterious for chromium carbides and beneficial for tantalum carbides. But this may lead to sustainability problems concerning resistance against hot oxidation and corrosion. With the same idea increasing the Ta content for given Co, Cr and C contents may favor TaC at the expense of chromium carbides. But this may lead to high cost prices. Concerning carbon, in presence of cobalt in quantity significant enough, its content may be rated in order to reserve carbon exclusively to form TaC carbides. These examples of effects on the characteristics of the carbides network were also suggested by the tendencies seen thanks to thermodynamic calculations. Even in a rather simple quinary system, many different levers are available to adjust microstructures to high temperature properties requirements. Thermodynamic calculations, with improved databases, may act as guidelines to select the most interesting chemical compositions.

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