

Thermodynamic and experimental study of a cobalt-based alloy strengthened by tantalum carbides

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ABSTRACT

Eutectic TaC carbides are known as being particularly efficient for the high temperature strengthening of cast cobalt-based superalloys. The usual contents in carbon and tantalum may be advantageously increased to progress in mechanical performances at elevated temperature. In this work a chromium rich (25wt.%Cr) TaC-reinforced cobalt-based superalloy was elaborated after preliminary thermodynamic calculations. The obtained microstructure, particularly rich in script-like shaped eutectic TaC mixed with the periphery part of the pre-eutectic dendrites of matrix, is furthermore free of any possible pre-eutectic TaC carbides. It lets hope very high creep resistance at high temperature, as preliminarily suggested by the rather high values of room temperature hardness.

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KEYWORDS

Cobalt alloy;
 Tantalum carbides;
 Thermodynamic calculations;
 As-cast microstructure;
 Hardness.

INTRODUCTION

Cobalt-based superalloys, mainly cast, are widely used since the middle of the last century for many high temperature applications^[1,2]. Their high mechanical resistance was initially given by the presence of heavy atoms solid solution and chromium carbides^[3]. Improvements in strengthening were thereafter obtained by promoting new more stable carbides “ often of the MC type “ as script-like eutectic carbides appeared mixed with matrix in grain boundaries at the end of solidification and as secondary carbides precipitated during optimized multiple step heat treatment. Since they cannot be really strengthened by aluminium-containing inter-

metallic particles as the famous single-crystal nickel-based alloys, adding to them several tens of weight percents in chromium is possible for allowing them well behaving in high temperature oxidation and corrosion^[4,5].

The most common MC carbides encountered in cast cobalt-based superalloys are tantalum carbides^[6], even if other types of monocarbides as NbC, ZrC^[7] or HfC^[7,8] were recently tested in such alloys. The volume fraction of TaC may be monitored by the carbon and tantalum contents, with as results moderate^[6] of very high^[9] fractions. A recent test in TaC enrichment in a cast chromium-rich cobalt-based alloys, with carbon and tantalum contents as high as 1 wt.% and 15 wt.% respectively^[9], led to very high

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fractions in script-typed eutectic TaC carbides but together with additional angular compact TaC carbides obviously appeared early during solidification as pre-eutectic crystals. These ones which tended segregating outwards induced an over-consumption of the costly tantalum element without real beneficial effect on the high temperature strength of the alloy. To prevent such loss in TaC but with however an increase in TaC-due reinforcement, a new alloy with increased but not too high contents in carbon and tantalum, always with an atomic Ta/C ratio equal to 1 to exclusively obtain TaC carbides, was considered in this work.

EXPERIMENTAL

The work started by thermodynamic calculations performed with the N version of the Thermo-Calc software^[10] for preliminarily know the successive solidification sequences and the final as-cast microstructure of the alloy. For that, Thermo-Calc worked with a database which initially contained the descriptions of the Co-Cr-C system and its sub-systems^[11-16] and which was enriched by the description of the binary and ternary sub-systems Ta-C, Co-Ta, Cr-Ta and Co-Ta-C^[17-19]. The theoretic appearance (and eventually disappearance) of the successive different phases were thus anticipated. The predicted mass fractions and chemical compositions of the different phases were obtained at successive temperatures and plotted from the liquidus down to a temperature low enough to allow considering that further microstructure change is now not possible (diffusion became too slow).

After having verified the theoretical microstructure may well respond to the requirements a quaternary Co(bal.)-25Cr-0.5C-7.5Ta alloy (all contents in weight percents) was elaborated by foundry by melting together, under inert atmosphere (pure Argon, 300mbars), pure elements (Co, Cr and Ta: Alfa Aesar, purity higher than 99.9 wt.%; C: graphite), by using a CELES high frequency induction furnace. Melting and solidification, occurred in the water-cooled copper crucible of the HF furnace, led to an ingot of about forty grams which was thereafter cut to provide samples for the microstructure charac-

terization and for the micro and macro indentation tests.

The sample for as-cast microstructure observations was embedded in a cold resin mixture (manufacturer ESCIL: resin CY230 + hardener HY956). It was polished with SiC papers from 240 to 1200 grit, with final polishing done using a textile disk enriched with 1 μ m alumina particles on the ultrasonically cleaned sample. The microstructure observations were performed using a Scanning Electron Microscopy (SEM JEOL JSM-6010LA), in the Back Scattered Electrons mode (BSE) with an acceleration voltage of 20kV. Whole frame and spot chemical analyses were performed using the Energy Dispersion spectrometry device of the SEM, for verifying the global chemical composition of the alloy, to identify the secondary phases, and to get the matrix's chemical composition. The image analysis tool of the adobe Photoshop CS software was used to measure the surface fractions of the carbides.

The indentation tests were carried out according to the Vickers method, with a 32g-load for the micro-hardness measurements (micro-indentor Reichert model D32) and with a 10kg-load for the macro-hardness ones (Testwell Wolpert). The micro-indentation runs aimed to try specifying the separate hardness of the alloy's matrix and of the interdendritic areas of TaC-matrix eutectic. The objective of the macro-indentation was acquiring the global hardness of the whole alloy.

RESULTS AND DISCUSSION

Thermodynamic calculations / microstructure evolution during solidification and solid state cooling

The first use of Thermo-Calc was to assess the melting range of the studied alloy. The obtained liquidus and solidus temperatures are respectively 1373°C and 1320°C. Further calculations, done every 10°C in the fusion/solidification interval temperature range and every 50°C in the solid state one, led to the first graph presented in Figure 1 in which one can see that the first crystallization at cooling from the liquid state is the one of the matrix. After a rather limited cooling during which the pre-eutectic

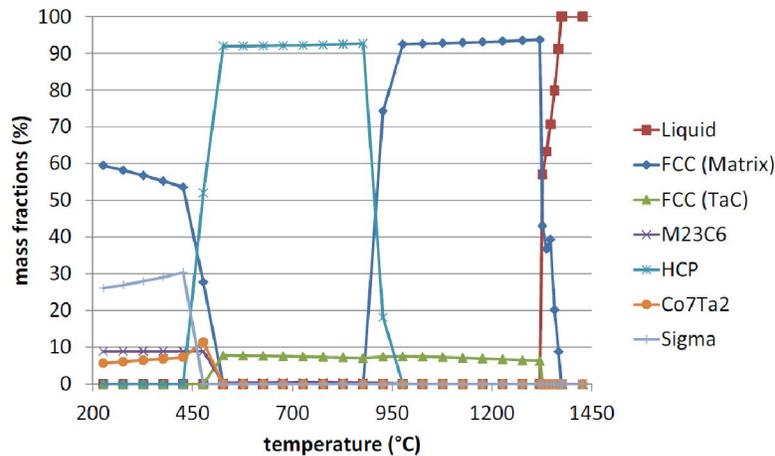


Figure 1 : Theoretic development of the microstructure of the studied alloy from the liquid state cooling (right side) down to very low temperature (left side), according to Thermo-Calc

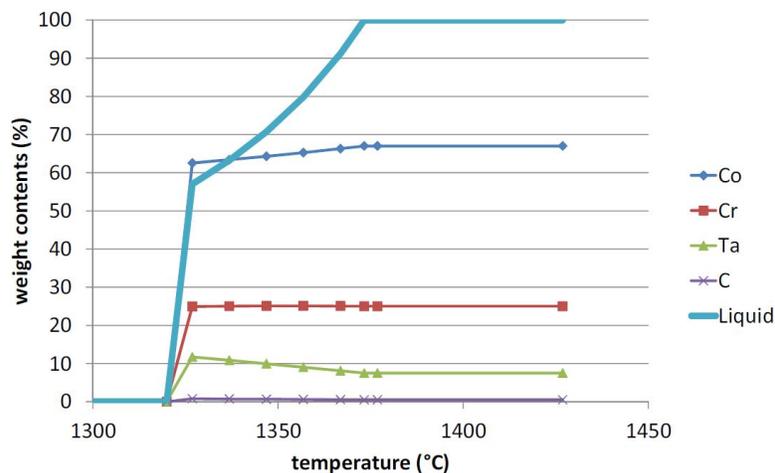


Figure 2 : Theoretic development of the microstructure of the studied alloy from the liquid state cooling (right side) down to very low temperature (left side), according to Thermo-Calc

austenitic matrix develops, the eutectic reaction takes place: remaining liquid \rightarrow FCC matrix + TaC. These ones finish to represent about 7-8 mass.% of the whole alloy and the microstructure does not evolve until the temperature reaches about 1200°C. A second type of carbides ($M_{23}C_6$) may appear but only as traces. The main microstructure change occurring at this temperature level is the allotropic transformation of the matrix, from FCC to HCP. During the following cooling this new hexagonal compact network exists, but only down to about 800°C, level of temperature at which a new change to FCC ought to occur, simultaneously with the appearance of a sigma phase and an intermetallic compound (Co_7Ta_2), and the disappearance of the TaC phase.

Thermodynamic calculations / chemical evolution of the main phases with temperature

During the cooling in the mushy zone the liquid progressively disappears before coming close to the eutectic temperature, in the neighbourhood of which its mass fractions suddenly falls. Its composition remaining mainly composed of cobalt (Figure 2), its tantalum and carbon contents increase during the pre-eutectic deposit of matrix (probably as dendrites), this leading to an enrichment of the interdendritic liquid in tantalum and carbon and finally the precipitation of a eutectic compound composed of matrix and TaC carbides.

The FCC cobalt-based matrix (Figure 3 top) contains almost the whole chromium in solid solution (about 27 wt.%, more than the 25 wt.%Cr of the whole alloy since a part of this one is composed of significant amount in TaC) and a maximum of almost 2wt.% Ta (as well as traces of carbon, 0.1 wt.%

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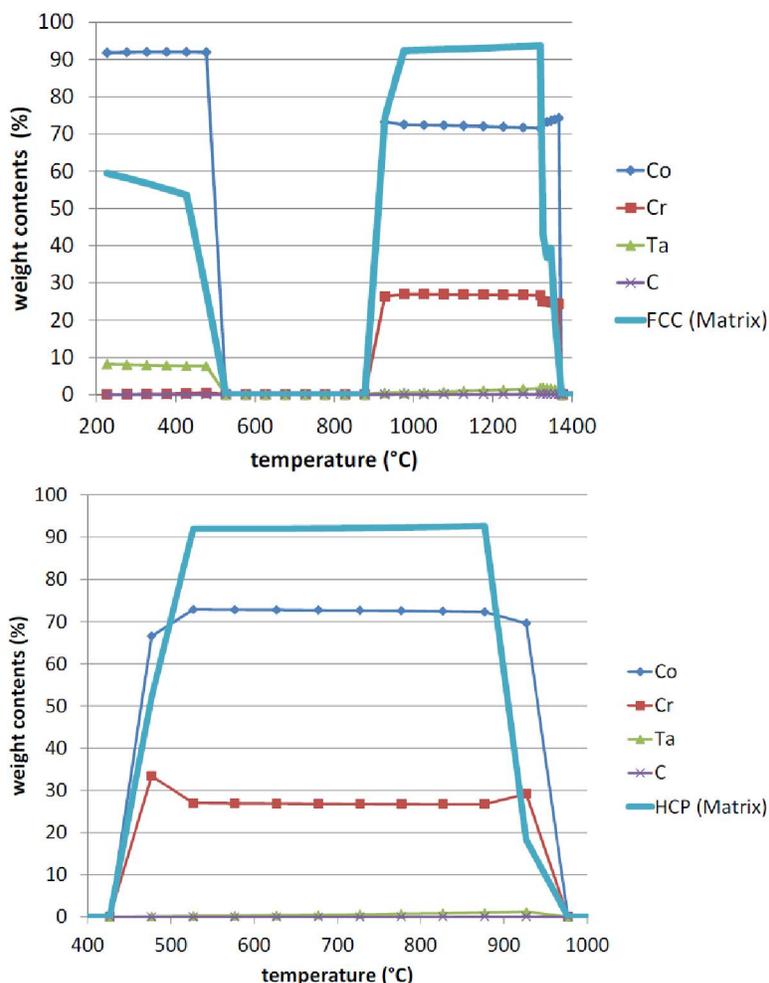


Figure 3 : Theoretic chemical evolutions of the FCC matrix (top) and of the HCP one (bottom) with temperature

and less). The HCP matrix (Figure 3 bottom), appearing instead the FCC one near 1200°C contains the same chromium quantity but less tantalum and carbon than the FCC matrix the Ta and C contents decreased during cooling because of the small additional deposition of TaC during solid state cooling.

The following evolution of the theoretic microstructure, not really interesting because it cannot really occur at such low temperature in practice, does not merit to be commented.

Thermodynamic calculations / chemical evolution of the carbide phases with temperature

The chemical compositions of the two types of carbides which ought to appear during cooling, TaC (end of solidification/eutectic reaction, then solid state) and $M_{23}C_6$ (only solid state) did not evolve in a wide range during cooling, especially the TaC car-

bides (Figure 4 top) the stoichiometry of which remains constant. In the $M_{23}C_6$ carbide phase (Figure 4 bottom) in which M simultaneously represents Cr as well as Co, the Cr/Co ratio increases during the cooling, Cr remaining the principal metallic element present in this carbide.

Thermodynamic calculations / chemical evolution of the low temperature phases

Concerning the two last phases supposed to appear at low temperature, the Co_7Ta_2 intermetallic phase (Figure 5 top) and the Topologically Close Packed sigma phase (Figure 5 bottom), the chemical composition of the first one does not vary with temperature while the Cr/Co ratio in the second one increases when temperature decreases.

As-cast microstructure of the real alloy

The microstructure of the obtained alloy in its

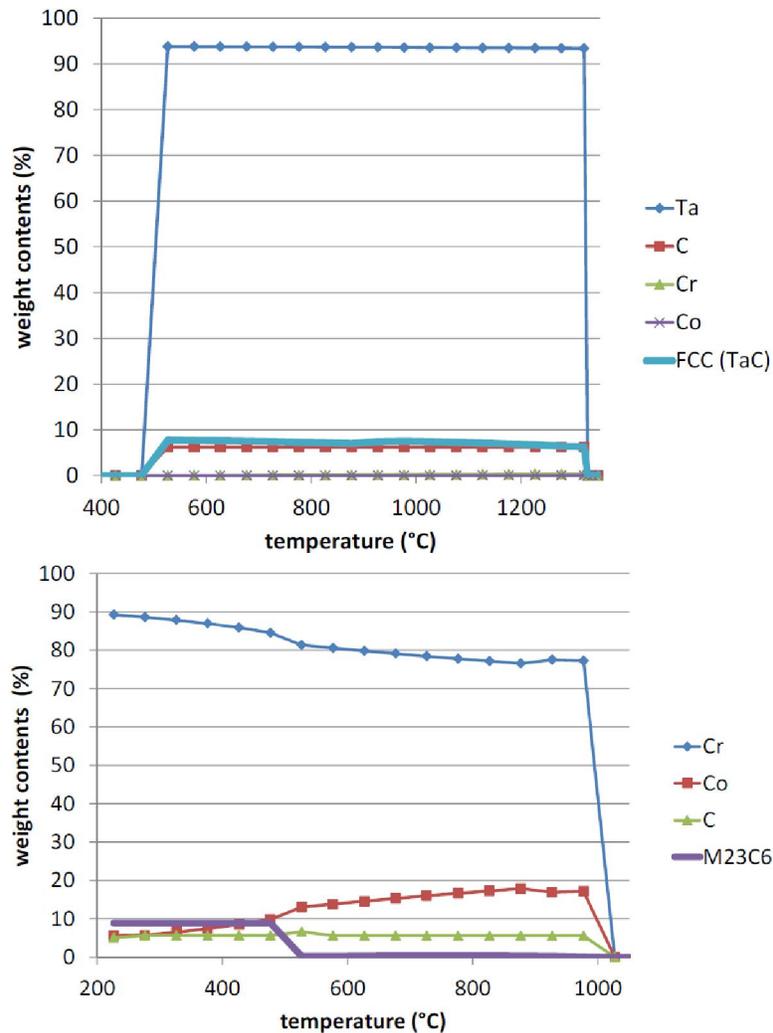


Figure 4 : Theoretic chemical evolutions of the tantalum carbide phase and of the chromium carbide one (bottom) with temperature

as-cast condition is illustrated in Figure 6. Its chemical composition acquired in whole frame at the $\times 1000$ magnification is 25.2 wt.%Cr and 10.2 wt.%Ta (over-estimated because its presence as mainly carbides), while the C content seems being well respected by looking at the obtained carbides' density (it cannot be measured using EDS because its too low mass and weight content). The matrix of the alloy is dendritic and the carbides are all present in the interdendritic spaces. The main ones are the tantalum carbides (high Ta content in EDS analysis) which appear white in BEC mode while there are here and there rare black chromium carbides (rich in chromium, EDS analysis).

The TaC carbides are script-shaped and mixed with matrix with which they form an eutectic compound. Their surface fractions were of about 6.90

± 0.85 surf.% TaC and 0.08 ± 0.12 surf.% Cr_{23}C_6 . Since the densities of the TaC and Cr_{23}C_6 carbides are respectively 14.5 and 6.97 g cm^{-3} ^[20], and the density of the whole alloy assessed by the volume divided by the mass of parallelepiped destined to creep tests is $8.57 \pm 0.14 \text{ g cm}^{-3}$ (supposed almost equal to the matrix one), it is possible to calculate, from these volume fractions, the corresponding mass fractions; this gives 11 mass.% of TaC and 0.06 mass.% of Cr_{23}C_6 .

The chemical composition of the matrix, assessed by EDS spot analysis, is 25.16 ± 0.17 wt.%Cr and 2.42 ± 0.23 wt.%Ta. It probably contains a part of carbon but it is unfortunately not possible to measure its content.

Indentation results

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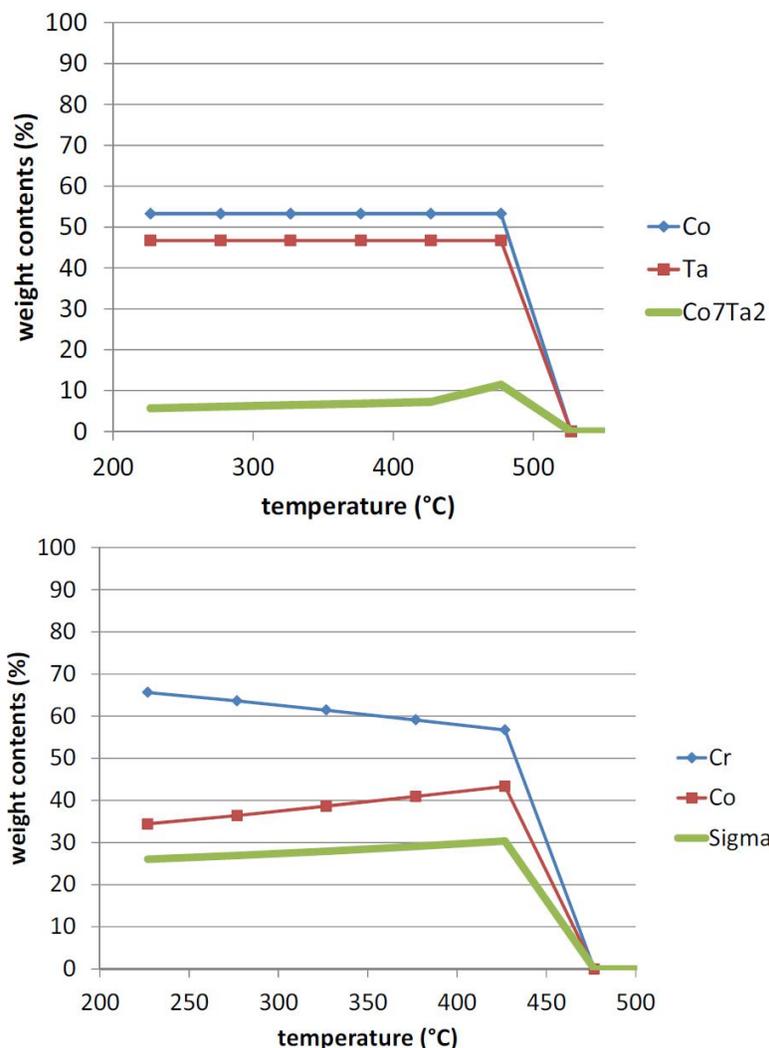


Figure 5 : Theoretic chemical evolutions of the intermetallic phase (top) and of the TCP one (bottom) with temperature

Micro-indentations were performed under 32g in several locations in the microstructures. The results were scattered but it was possible to share them between two packs of values, a pack of high ones and a pack of low ones. The second pack, which may be attributed to the matrix, was characterized by an average hardness of $342 \pm 18 \text{ Hv}_{32\text{g}}$ while the first one, characterized an average hardness of $428 \pm 39 \text{ Hv}_{32\text{g}}$, may be affected to the TaC-matrix eutectic compound. The macro-indentation test led to $370 \pm 12 \text{ Hv}_{10\text{kg}}$, as is to say between the micro-hardness values of the matrix and of the eutectic {TaC + matrix} areas.

General commentaries

The preliminary calculations showed first that

the first crystals to appear at the early beginning of solidification would be the matrix and that the eutectic carbides will be only eutectic ones. This was effectively seen in the as-cast microstructure in which no pre-eutectic angular compact TaC carbides were visible, in contrast with what was previously observed with a chromium-rich cobalt-based alloys with double contents in both carbon (1 wt.% C) and tantalum (15 wt.% Ta)^[9]. Thus the whole quantity of the tantalum introduced in the alloy is exploited (no loss of TaC carbides by induction-induced centrifugal migration as for the pre-eutectic ones in^[9]), mainly as carbides – exclusively script-like eutectic in the interdendritic spaces where their strengthen the cohesion between dendrites – and partly as heavy atoms dissolved in matrix which they strengthen by

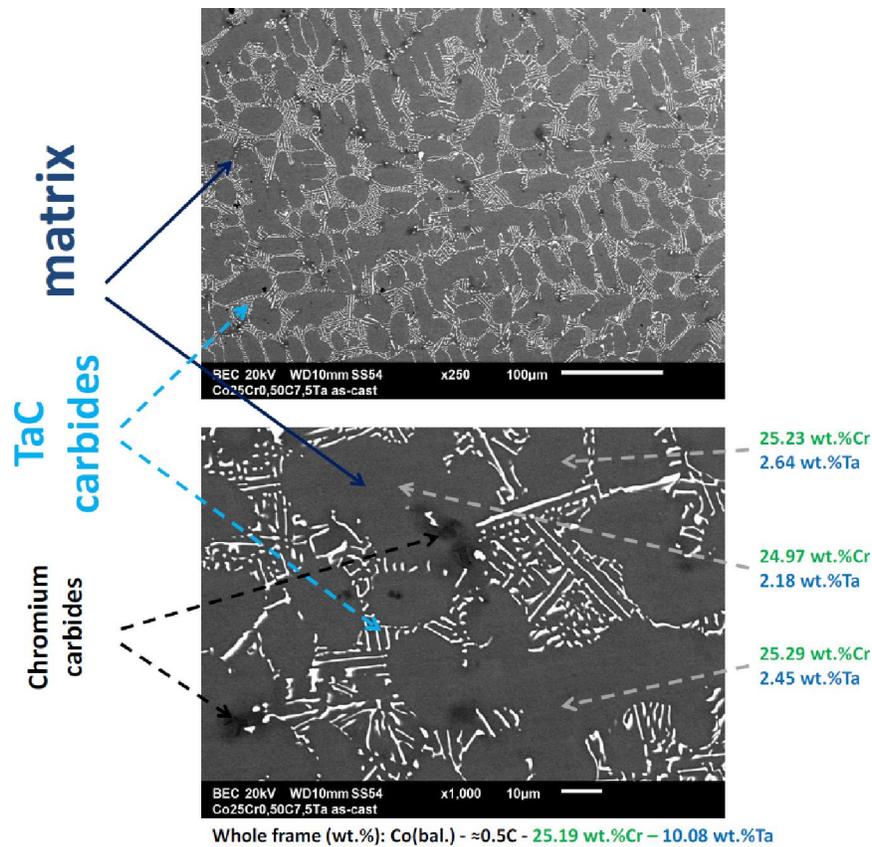


Figure 6 : As-cast microstructure of the studied alloy for two magnifications (SEM/BEC micrographs; EDS whole frame and spot analysis results)

solid solution effect. The costly tantalum is fully used for reinforcement. The obtained mass fractions are a little higher than predicted by Thermo-Calc (11 mass.% against the 6-8 calculated for the intermediate temperature range) while the real Ta content in matrix is higher than predicted by thermodynamic calculations: 2.4 wt.% Ta in matrix against the calculated values (lower than 2 and even 0.5 depending on the considered temperature).

Concerning the room temperature hardness, despite the high difference of applied load (ratio of one thousand) all the hardness results are remarkably consistent and it will be interesting to verify if the macro-hardness can be considered as resulting from a law of mixture with the volume fractions of matrix and of eutectic compounds as coefficients.

CONCLUSIONS

With carbon content and tantalum content as high as 0.5 and 7.5 wt.% respectively, this {Co-

25wt.%Cr}-based cast alloy contains more eutectic TaC carbides than similar alloys with only 0.4 and 6wt.% of C and Ta, and it is still free from any pre-eutectic carbides in contrast with an alloy with 1 and 15 wt.% of C and Ta. Necessarily it costs a little more than the first alloy evoked just before, but one can guess that its high mechanical properties are better, thanks to this efficiently reinforcing dense interdendritic eutectic TaC carbides network, as suggested here by the rather high values of room temperature hardness. This will be soon verified by high temperature creep tests.

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