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Thermodynamic study of the mushy zone of cobalt-based superalloys. Part 1: Case of a low carbon alloy

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ABSTRACT

In order to better know the high temperature metallurgical state of a low-carbon chromium-rich cobalt-based superalloy strengthened by carbides of chromium and tantalum, as well as to test a thermodynamic modelization tool for such ranges of temperature and of alloy’s chemical composition, two types of experiments were done. First an exposure of a selected alloy at high temperature was done and finished by a water-quenching allowing characterizing its high temperature microstructure. Second thermodynamic calculations were performed for comparison with the experiments. Qualitatively the agreement was rather good (the initial microstructure of the alloy and its partially molten state at 1300°C were both predicted and observed). But mismatches appear in the quantitative field, for example concerning the volume or mass fractions of liquid at the temperature of test. However the metallurgical data obtained for the studied alloy at very high temperature by respect to its melting range, as well as the transformations of the microstructure during quenching, are of good interest.

KEYWORDS

Cobalt alloy;
Chromium carbides;
Tantalum carbides;
Mushy zone;
Thermodynamic calculations.

INTRODUCTION

Cobalt-based superalloys, the most often elaborated by casting (and eventually thereafter plastically deformed to obtain wrought versions), represent an important family of high temperature alloys[1], even if γ/γ' nickel-based alloys – notably in their single-crystal versions – are better placed among the most efficient superalloys for very high temperature applications[2,3]. If some of them are {solid solution} – strengthened, most of cobalt-based superalloys are reinforced by carbides. These ones may appear at the end of solidification (primary carbides) and/or they may be obtained by special heat-treatment (secondary carbides). The first ones, which precipitate at the end of solidification in most cases, often form a eutectic compound with the matrix, this leading to a lowering of the melting point of the alloys. Due to that, the concerned superalloys are not so refractory as the {eutectic carbides} - free ones and they are more threatened by a possible partial fusion in case of too high working temperature. To better know the risks of such problem of partial fusion, which can be extremely detrimental for the high temperature mechanical properties as well as for the high temperature oxidation behaviour[4,5], thermodynamic modelling may be of a good help to anticipate what may occur at high temperature, carbide degeneration or appearance of liquid.

The purpose of the present work is, in this first part, testing a thermodynamic modelling tool in the case of a low carbon alloy before using it to expertise some pieces made of similar low carbon cobalt alloy and having obviously suffered partial fusion in service and then too early ruin than expected. The thermodynamic prevision tool tested here is the Thermo-Calc software and a database supposed to be able to predict the metallurgical states at higher temperature of austenitic nickel-stabilized chromium-rich cobalt-based alloys containing not only carbon and tantalum, but also tungsten, an element participating to the {solid solution} – strengthening but also being possibly involved in the chemical composition of chromium carbides if any.

EXPERIMENTAL DETAILS

The cobalt-based superalloy selected for this work

The superalloy chosen for this first part of the work (chemical composition given in TABLE 1) was prepared as a liquid alloy (about 20 kg) melted from pure metals and ferroalloys in a vacuum - inerted induction furnace, and thereafter poured in a sand mould. After total (slow) solidification, the alloys, characterized by a rather coarse microstructure, underwent a thermal treatment composed of a first high temperature stage (the solutionning one) long enough to allow both chemical homogenization for the microstructural coarseness, and second a precipitation stage allowing the precipitation of fine secondary carbides in the matrix to enhance the creep resistance by obstructing the dislocations' movements.

TABLE 1 : Targeted chemical composition for the alloy under study (in wt.%).

Co	Ni	Cr	C	Ta	W
Bal.	8.5	29	0.4	3.0	5.8

Exposures of the alloy to high temperature and metallographic preparation

A part of about 1 cm^3 in volume was cut in one of the samples obtained as described above (after its double (solutioning + precipitation) heat-treatment. The part was entered in the hottest zone of a muffle furnace (atmosphere: laboratory air) to be exposed to 1300°C for 5 hours. Thereafter the part of alloy was extracted from the furnace and quickly immersed in water at room temperature, to freeze the microstructure existing at 1300°C. The part of alloy was thereafter cut, embedded in a cold resin mixture (manufacturer ESCIL: resin CY230 + hardener HY956), polished with SiC papers from 240 to 1200 grit, with final polishing done using a textile disk containing 1µm alumina particles, until obtaining a mirror-like surface state.

Microstructure observations and characterization

The observations of the microstructure supposed stabilized at 1300°C after the five hours spent at this very high temperature were done using a JEOL JSM7600F Scanning Electron Microscope (SEM) and their general or local chemical compositions were measured using its Energy Dispersion Spectrometry (EDS) device. The same apparatus was also used for the pinpoint measurements of the chemical composition of the matrix.

The micrographs were thereafter worked using the Photoshop CS software, first to delimit the frozen zones (liquid zones existing at 1300°C and rapidly solidified with a very fine microstructure due to the quenching in water). The cumulated surface fractions of the preliminarily delimited frozen zones were measured using the image analysis tool present in Photoshop.

The thermodynamic modelling tool evaluated in this work

Thermodynamic calculations destined to be compared to the metallurgical characteristics of the overheated superalloy were performed with the N-version of the Thermo-Calc software[6], working with the data contained in a database built from the SSOL[7] database already present in the initial package. This initial database contained the descriptions of the Co-Cr-C system and its sub-systems[8-13] as well as systems involving the tungsten element (W), and it was necessary to enrich it with the descriptions of the binary and ternary sub-systems involving the tantalum element: Ta-C, Co-Ta, Cr-Ta and Co-Ta-C[14-17].

The calculations which were performed aimed to obtain mass fractions of liquid for the thermodynamic equilibrium state at 1300°C, its chemical composition, the chemical composition of the matrix, in order to compare all these data to the corresponding measured values.

RESULTS

SEM examination of the alloy's microstructure before exposure to high temperature

The initial microstructure of the alloy (just after casting and solutioning & precipitation heat-treatment), illustrated in Figure 1, can be described as follows: this is a dendritic structure with interdendritic spaces occupied by either a fine eutectic compound involving matrix and chromium carbides (of the $M_{23}C_6$ stoichiometry), or by a coarser eutectic compound composed of matrix and "script" tantalum carbides (TaC).

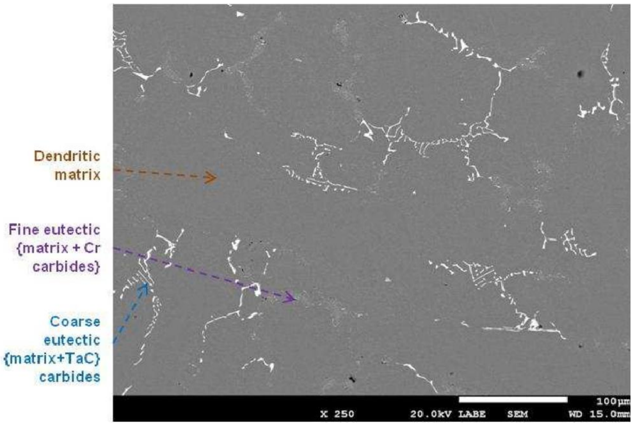

Figure 1 : The initial microstructure of the alloy (after solutioning + precipitation heat-treatment).

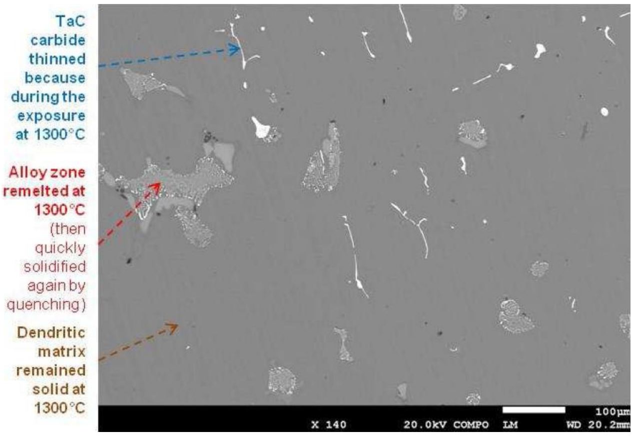

Figure 2 : Microstructure state of the alloy (after 5h of exposure to 1300°C and water-quenching).

The chemical composition of this alloy was determined by EDS measurements, on several areas randomly selected in the microstructure and at a magnification allowing to stay representative of the whole alloy. The obtained results, given in TABLE 2, show that the wished composition was seemingly respected, except the existence of iron which was brought by the use of ferroalloys. By considering in addition that Fe is present with a rather low content (compared to cobalt and nickel, with which iron has a similar (very low) carbide-former power), it was thus considered that the measured chemical composition is very close to the one initially wished, the latter one remaining able to be used for the thermodynamic calculations.

TABLE 2 : Average chemical composition as obtained from EDS measurements (four times on randomly selected areas of about 840 × 620 µm²); chemical composition of the matrix.

Main elements	Areas (alloy's composition)		Matrix (pinpoint)
	Average value	Standard deviation	
Co	Bal.	/	Bal.
Ni	9.1	± 0.4	9.0
Cr	29.6	± 0.5	29.9
C	0.4 (targeted content)	/	/
Ta	3.4	± 0.4	/
W	6.2	± 0.4	4.8
Fe	2.2	± 0.2	2.2

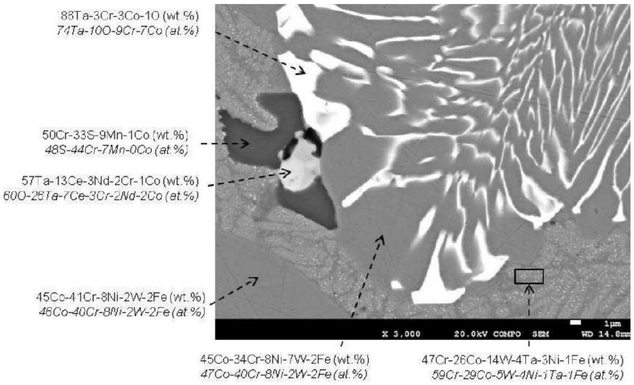

Figure 3 : Examples of various phases having precipitated in {out of equilibrium} conditions during the quenching; chemical compositions of some of them as analyzed by EDS (carbon excepted).

SEM examination of the alloy's microstructure after exposure to high temperature and quenching

The microstructural state of the alloy frozen from

1300°C after its exposure for 5 hours at this temperature is illustrated in Figure 2. The microstructure, still dendritic of course, has however evolved concerning the natures of its interdendritic spaces. The eutectic compounds initially existing here have been replaced by non-equilibrium solid areas displaying both a more compact and rounder morphology and a very fine microstructure. One can guess that the very fine microstructure zones results from the extremely rapid re-solidification of the eutectic zones (which were re-melted since they are the less refractory ones in the alloy) due to the quenching operation, the partial melting of these areas at 1300°C being responsible to the loss of the initially elongated shapes of these eutectic domains. One can see also some white particles (TaC carbides) that it is easy to interpret as the results of a morphology change of the eutectic tantalum carbides initially present with a rather high interfacial energy due to their "script"-like shapes developed during the first slow solidification. In fact, some of the {re-melted/quickly re-solidified} zones are rather complex, as illustrated in Figure 3 in which several phases with various chemical compositions can be present together. Foreign elements detected in EDS (e.g. Ce) possibly came from the preliminary treatment of the liquid metal (Mischmetall for de-oxidizing the bath).

TABLE 3 : Metallurgical state of the alloy at 1300°C according to Thermo-Calc (calculations performed from the average chemical composition given in TABLE 1.

Phase	Mass fraction	Phase's composition					
		Co	Ni	Ta	Cr	W	C
FCC matrix	54.71%	55.98	9.32	0.84	29.13	4.66	0.06
Liquid	45.29%	45.79	8.86	6.47	30.17	7.95	0.77

First thermodynamic calculations

The presence of two types of carbides ($M_{23}C_6$ and TaC) in addition to the {Co(Ni,Cr,W,C,Ta)} – based solid solution in the as-cast then heat-treated alloy after the slow cooling (massive piece and air-cooling) down to room temperature was predicted by first thermodynamic calculations, as illustrated by the phase diagrams displayed in Figure 4. The upper one (A), plotted between 1400 and 1600 K (and between 1 and 5 wt.% Ta), is enlarged below (1520 – 1550 K) for better seeing the high temperature domains (B):

- Liquid and matrix (domain 2)
- Liquid + Matrix + M_7C_3 carbides (domain 5)
- Liquid + Matrix + TaC carbides (domain 6)
- Liquid + Matrix + M_7C_3 carbides + TaC carbides (domain 7)
- Liquid + Matrix + $M_{23}C_6$ carbides + TaC carbides (domain 8)
- Matrix + M_7C_3 carbides + $M_{23}C_6$ carbides + TaC carbides (domain 9)
- Matrix + TaC carbides + M_7C_3 carbides (domain 3)
- Matrix + TaC carbides + $M_{23}C_6$ carbides (domain 1)
- Matrix + TaC carbides + M_7C_3 carbides + $M_{23}C_6$ carbides (domain 4)

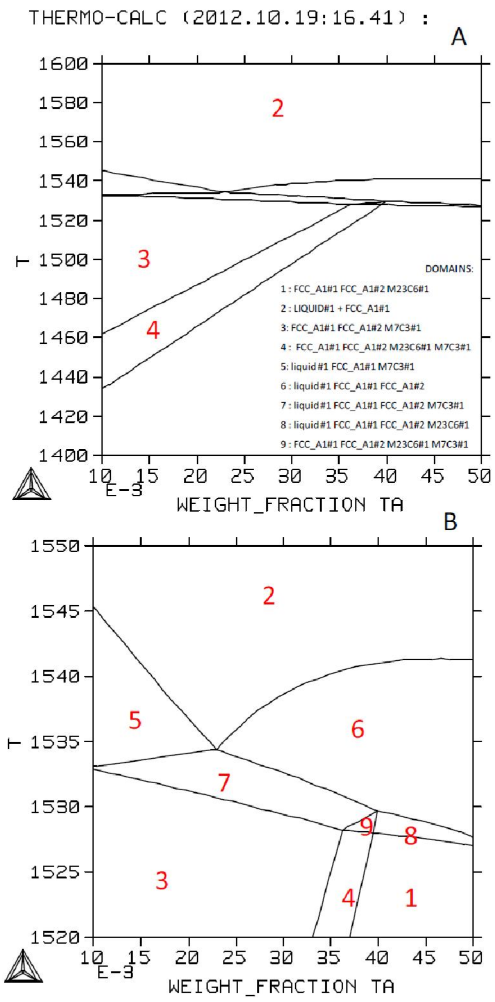

Figure 4 : A→ High temperature part (1400 – 1600 K) isopleths of the phase diagram computed between 1 and 5 wt.%Ta for a base chemical composition of Co(bal.)-29Cr-8.5Ni-0.4C-5.8W; B→ enlarged view of the top diagram (A).

For 3wt.% Ta the solidification followed by the solid state cooling should lead effectively to the two types of carbides: eutectic M_7C_3 thereafter transformed in $M_{23}C_6$, and eutectic TaC.

Calculations were also performed for determining the thermodynamic stable state at 1300°C. At such temperature (about 1573 K) which corresponds to domain 2 (Liquid + Matrix) according to the phase diagrams presented in Figure 3, the alloy should be partially re-melted, with notably the disappearance of the two types of eutectic areas (eutectic matrix + $M_{23}C_6$ and eutectic matrix + TaC), with instead the appearance of a liquid especially rich in carbon (C) and in carbide-former elements (Ta, Cr, W), as shown in the last line of TABLE 3.

Further, according to TABLE 3, the two phases matrix and liquid would be present with similar volume fractions, even if the mass fraction in liquid phase is slightly lower than the mass fraction of matrix. Indeed, due to a volume mass slightly higher for matrix than for liquid the two mass fractions may lead to similar volume fractions then surface fractions).

TABLE 4 : Theoretical microstructure (number and nature of the existing phases and of their mass fractions) just at the end of solidification of the liquid phase (the composition of which is assumed to have remained the same as the one presented in TABLE 3 because of the very high cooling rate (negligible diffusion).

<table>
<tr><th colspan="3">Solidus temperature (K/°C)for the chemical compo. given in TABLE 3:</th><th colspan="3">1517.35K / 1244.20°C</th></tr>
<tr><td colspan="6">↓ Microstructure of the frozen liquid zones just after solidification, at 1244.20°C ↓</td></tr>
<tr><td colspan="3">Phase</td><td colspan="3">Mass fraction</td></tr>
<tr><td colspan="3">Liquid</td><td colspan="3">0%</td></tr>
<tr><td colspan="3">FCC matrix</td><td colspan="3">87.79%</td></tr>
<tr><td colspan="3">TaC carbides</td><td colspan="3">6.10%</td></tr>
<tr><td colspan="3">$M_{23}C_6$ carbides</td><td colspan="3">6.11%</td></tr>
<tr><td colspan="6">Chemical composition of the matrix in the frozen liquid zones</td></tr>
<tr><td>Co</td><td>Ni</td><td>Ta</td><td>Cr</td><td>W</td><td>C</td></tr>
<tr><td>51.37</td><td>10.09</td><td>1.02</td><td>29.02</td><td>8.44</td><td>0.07</td></tr>
</table>

If Thermo-Calc also allowed to calculate the theoretical mass fractions and chemical compositions of the different phases at a given temperature (1300°C in TABLE 3) if the metallurgical state may be considered close to the thermodynamic state, it can be also used to try interpreting (much less quantitatively of course) the microstructures developed during a rapid cooling. Calculations were thus performed first for determine the solidus temperature corresponding to the experimentally measured chemical composition of the alloy (measured by EDS: TABLE 2), and second to get an approached value of mass fraction for each solid phase by supposing that no solid state evolution was thereafter possible because of the great cooling rate due to water quenching. This led to the results presented in TABLE 4.

Comparison between metallographic results and calculated results

First, the micrographs taken with the SEM in Back Scattered Electrons (BSE) mode were re-worked in order to color in white the zones obviously re-melted after 5 hours at 1300°C then re-solidified with a fine structure (TaC carbides finely mixed with a part of ma-

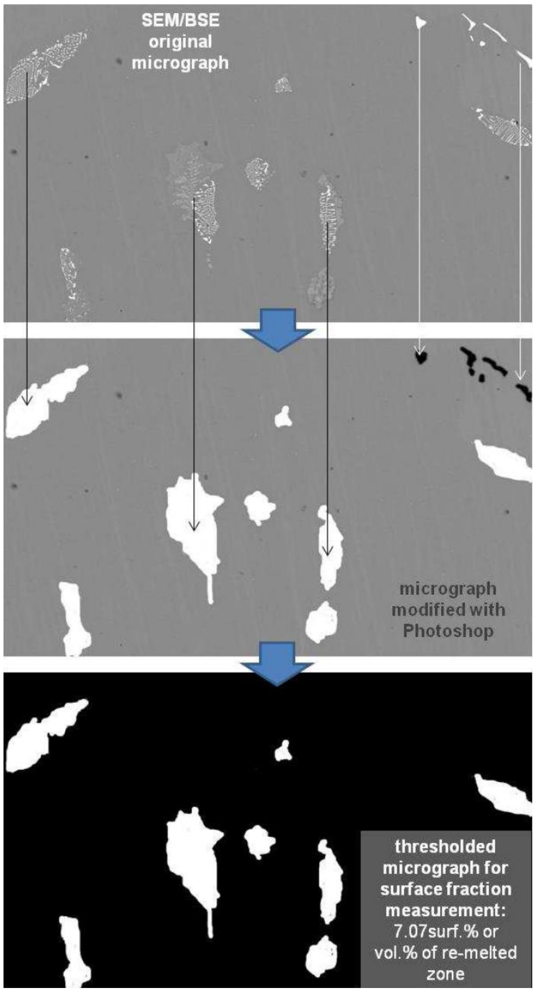

Figure 5 : Modification of a SEM/BSE micrograph under Photoshop before image analysis.

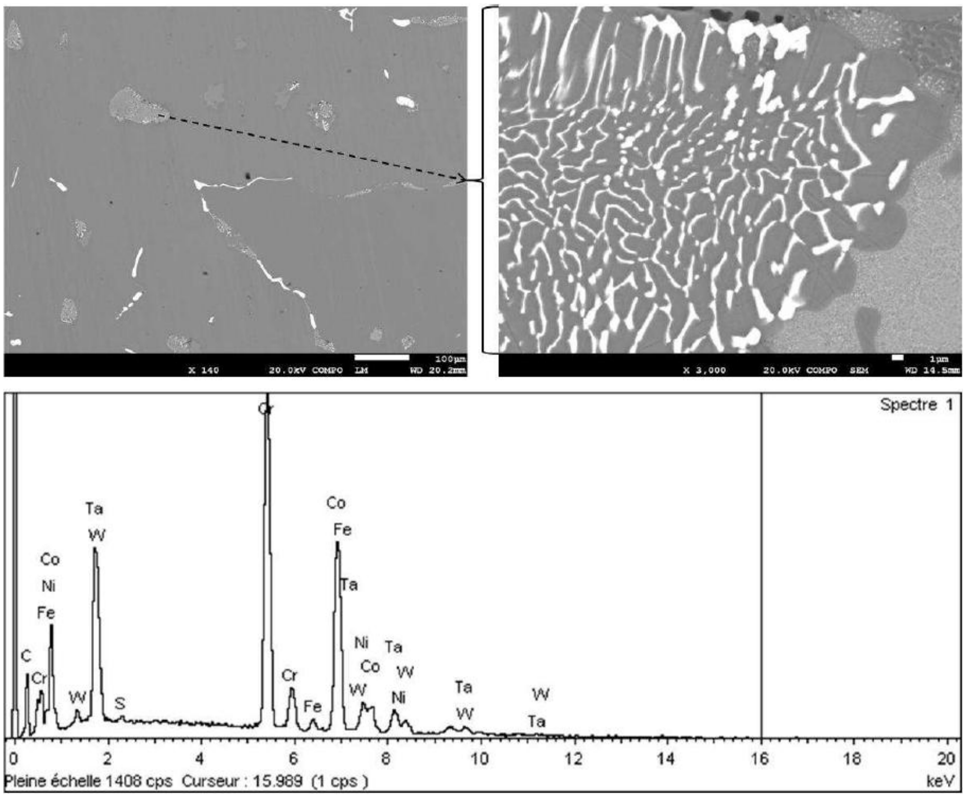

Figure 6: EDS spectrum acquired in a first {re-melted/re-solidified} zone: 33.2Co-31.5Cr-15.9Ta-9.3W-5.0Ni (+ minor elements: Fe, S …) in weight percents.

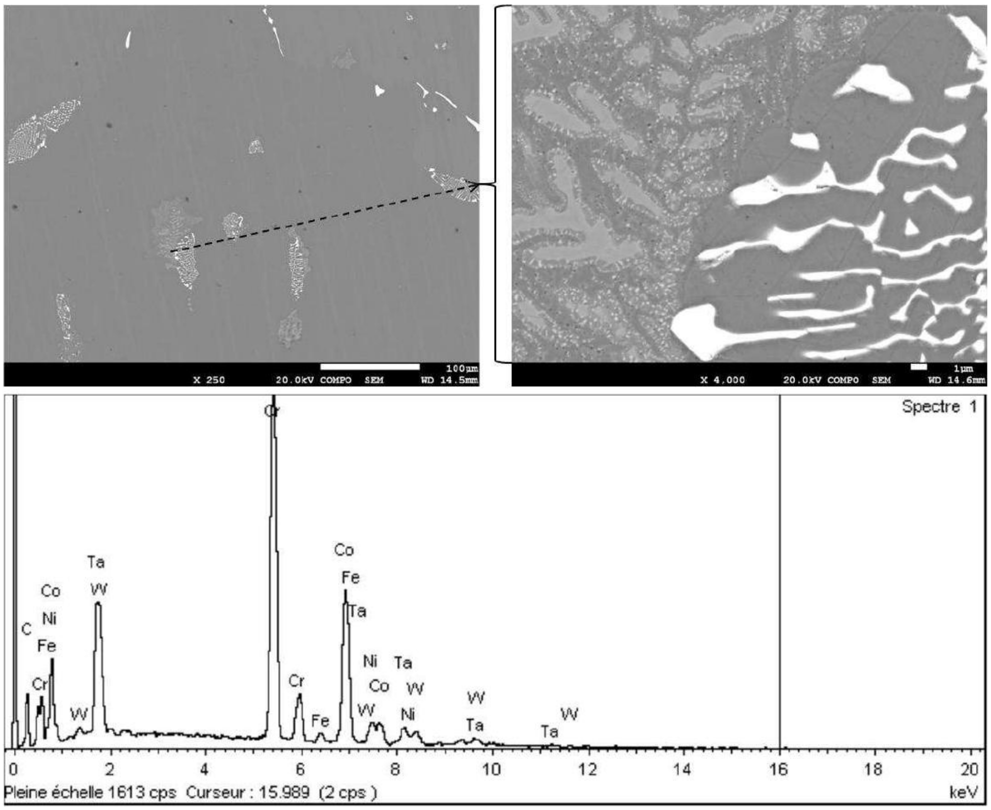

Figure 7: EDS spectrum acquired in a second {re-melted/re-solidified} zone: 31.2Co-36.6Cr-11.2Ta-10.4W-4.5Ni (+ minor elements: Fe …) in weight percents.

trix, other adjacent domains), and to color in black the other TaC carbides obviously belonging to the still solid part of the microstructure of the alloy (illustrated in Figure 5).

The surface or volume fraction obtained for the zones re-melted at 1300°C is equal to 6.22 ±1.5 % (average of three values ± standard deviation). This is significantly lower than the volume fractions – which can be taken as almost equal to the mass fractions in first approximation (volume masses probably rather close to one another) – which were previously predicted by Thermo-Calc.

Second, it was attempted to analyze the chemical composition in a {re-melted/re-solidified} zone by EDS. In the one considered in Figure 6, it appeared that such zone may be especially rich in chromium, tantalum and tungsten, this resulting from the re-melting of both $(Cr,W)_{23}C_6$ and TaC carbides with a part of matrix. Similar results were found in a second {re-melted/re-solidified} zone (Figure 7) which obviously contains quantities of Cr, W, Ta not far from the previous values. One can note that the chemical composition of these two zones are, except tantalum which seems very present in reality (content equal to the double of the calculated one), rather close to the liquid composition calculated by Thermo-Calc and presented above in TABLE 3.

Concerning this calculated composition of the liquid existing at 1300°C (in which features the carbon content which cannot be analyzed by EDS in the two re-melted and re-solidified zones considered above), it is possible to assess both the solidus temperature of this sole phase liquid (the elements of which cannot have time enough to diffuse in the matrix during water-quenching) and the microstructure which may be obtained at this local solidus temperature. For this composition {Co(bal.) – 8.86 Ni – 6.47 Ta – 30.17 Cr – 7.95 W – 0.77 C}, calculations lead to a local solidus temperature equal to 1244.2°C and, at this temperature, 0% of liquid, 87.79% of matrix, 6.10% of TaC carbides and 6.11% of $M_{23}C_6$ carbides (TABLE 4), which is logically much more than the fractions of carbides in the whole alloy just after its solidification ($T_{sol\ alloy}$ = 1252.58°C i.e. 1253°C, 94.57 mass.% of matrix, 2.71 mass.% of TaC and 2.73 mass.% of $M_{23}C_6$), since the carbides of the microstructure are localized in these areas.

To finish one can compare the chemical composition of the matrix between EDS measurements and calculations: there is a rather good agreement since the one determined by EDS is (TABLE 2): Co(bal.)-29.9Cr-9.0Ni-4.8W-0 (not measurable)Ta against, for calculations performed for 1300°C: Co(bal.)-29.1Cr – 9.3Ni-4.66W-0.84Ta (for Ta: lower than the EDS limit of detection).

General commentaries

Thus, qualitatively, the thermodynamic calculations tool which was tested here gave good results since the initial microstructure was faithfully given by calculations (matrix + $M_{23}C_6$ carbides + TaC carbides) and the good metallurgical state (matrix + liquid) was effectively found for 1300°C (with in addition a chemical composition of matrix in accordance with EDS measurements). Unfortunately the (experiments <-> calculation) agreement was worse quantitatively, notably concerning the mass fraction or volume fraction of liquid at 1300°C. The mismatch can be explained either by a time maybe not long enough spent at 1300°C (one can wonder if the alloy had really reached its thermodynamic stable state at this temperature) or by a weakness of the database for the high temperature and/or the description of the semi-molten states. However, in its actual state, the thermodynamic calculation tool maybe used for obtaining first indications concerning the states of low carbon cobalt-based alloys (of similar compositions) at high temperature close to their melting point. In contrast, all the experimental observations done in this work and concerning the metallurgical behavior of this alloy are potentially interesting for many classical cobalt-based alloys rich in chromium and containing carbon, tantalum and tungsten in usual contents.

CONCLUSIONS

The low carbon cobalt-based superalloy studied here presents a refractoriness which is rather limited since significantly lower than 1300°C. Even for a so complex chemical composition thermodynamic calculations have shown that a partial melting may occur, despite that the mass or volume fractions determined for the studied temperature were not accurate. Although these first results being not very good, the thermodynamic calculation tool used here has proved that it can be of a great utility in its present state. However some improvements are required to obtain better predictions. It will be tested in the case of a high-carbon cobalt-based alloy in the second part[18] of this work, in order to explore its efficiency in case of much high fractions of carbides.

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REFERENCES

[1] A.M.Beltram; Cobalt-base alloys, 135; in C.T.Sims, N.S.Stoloff, W.C.Hagel (Eds); Superalloy II – High temperature materials for aerospace and industrial power, John Wiley-Interscience, New York, **(1987)**.
[2] C.T.Sims, W.C.Hagel; The superalloys, John Wiley & Sons, New York, **(1972)**.
[3] E.F.Bradley; Superalloys: A technical guide, ASM international, Metals Park, **(1988)**.
[4] P.Berthod; Computer coupling of phase diagrams and thermochemistry, **32**, 492 **(2008)**.
[5] P.Berthod; Materials science, An Indian Journal, **5(1)**, 55 **(2009)**.
[6] Thermo-Calc version N: Foundation for computational thermodynamics stockholm, Sweden, Copyright, **(1993, 2000)**.
[7] SGTE: Scientific group thermodata europe database, update, **(1992)**.
[8] A.Fernandez Guillermet; Int.J.Thermophys., **8**, 481 **(1987)**.
[9] J.O.Andersson; Int.J.Thermophys., **6**, 411 **(1985)**.
[10] P.Gustafson; Carbon, **24**, 169 **(1986)**.
[11] A.Fernandez Guillermet; Z.Metallkde, **78**, 700 **(1987)**.
[12] J.O.Andersson; Calphad, **11**, 271 **(1987)**.
[13] A.Fernandez Guillermet; Z.Metallkde., **79**, 317 **(1988)**.
[14] K.Frisk, A.Fernandez Guillermet; J.Alloys Compounds, **238**, 167 **(1996)**.
[15] Z.K.Liu, Y.Austin Chang; Calphad, **23**, 339 **(1999)**.
[16] N.Dupin, I.Ansara; J.Phase Equilibria, **14**, 451 **(1993)**.
[17] L.Dumitrescu, M.Ekroth, B.Jansson; Metall.Mater. Trans.A, **32A**, 2167 **(2001)**.
[18] P.Berthod, E.Conrath; Materials Science: An Indian Journal, Accepted Paper.