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Thermodynamic study of the mushy zone of cobalt-based superalloys. Part 2: Case of a high carbon alloy

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ABSTRACT

After having controlled the reliability of the thermodynamic modelization tool in the first part of this work, thermodynamic calculations were here used again, this time to try finding the value of the high temperature known by a piece made of a cobalt-based superalloy which seemingly partially melted. For that the chemical compositions of the matrix and of the molten then re-solidified areas were measured by Energy Dispersion Spectrometry, as well as the surface fractions. Thermodynamic calculations performed from the global chemical composition of the whole alloy also controlled by EDS allowed, by comparison between the calculated results and the metallographic ones, to assess the temperature at which the alloy was exposed. A very good agreement was found between the different temperatures suggested by the fractions of re-solidified molten areas and of the tantalum carbides having remained solid during H.T. exposure, by the chemical compositions of the matrix and of the re-solidified molten areas, with however some exceptions. Thus, the value determined for the exposure temperature appeared rather reliable, and the thermodynamic calculation package efficient as an expertise tool for such post-mortem determination.

KEYWORDS

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

INTRODUCTION

The cobalt-based superalloys are sometimes used for high temperature applications[1], for example where a good resistance against high temperature corrosion requires important chromium contents in not-coated refractory alloys[2], as this can be the case for some of the hottest parts in aero-engines possibly in contact with liquid CMAS or for some industrial pieces forming molten glasses[3]. The cobalt-based superalloys are usually elaborated by foundry, a first operation eventually followed by thermo-mechanical working to obtain forged versions of the same alloys, and, even if many cobalt alloys for high temperatures only reinforced by solid solution hardening also exist, most of them are strengthened by carbides: primary carbides appeared in the grain boundaries and interdendritic spaces during the solidification of the alloy, or secondary dispersed fine carbides homogeneously precipitated in the matrix[4].

The presence of carbon in such alloys is known to cause a significant lowering of their refractoriness since, although the carbides formed are efficient reinforcing particles allowing maintaining high mechanical properties at high temperatures, the ones of these carbides which precipitated at the end of solidification (after the development of the dendritic network) are generally eutectic carbides, more precisely forming a low-temperature melting eutectic compound with the matrix if some of these carbides involve a part of the chromium existing in the alloy. Notably, when the carbon content is close to the upper limit of the contents' range usually concerning the carbides-strengthened cobalt-based superalloys, the concerned alloys may be threatened by a possible partial melting if the service local or global temperature accidentally jumps to a too high level even for a short time.

In the present work a piece made of a chromium-rich cast cobalt-based superalloy mechanically reinforced both by solid solution strengthening (tungsten and tantalum atoms) and by many chromium+tungsten carbides and tantalum carbides (due to a carbon content particularly high: around 1 wt.%C), was heated to a temperature especially high during several hours before a rapid cooling occurred. Effectively the microstructure examination of a part of this piece showed, after a metallographic preparation, several areas having seemingly melted then rapidly solidified. In order to better know the high temperature shortly encountered by the alloy, it was attempted to use the thermodynamic calculation package previously tested in the first part of this work[5] which appeared as able to give rather good results concerning the mushy zone of cobalt-based superalloys containing the same chemical elements.

EXPERIMENTAL DETAILS

Metallographic preparation and observation of the over-heated piece made of cobalt-based superalloy

A part of about 0.5 cm^3 was cut in the {about 20kg}-weighing part of the studied piece, then embedded in a cold resin mixture (resin CY230 + hardener HY956, from ESCIL), grinded / polished with SiC papers (grit from 120 to 1200), ultrasonically cleaned and thereafter finely polished using a textile disk enriched with 1μm alumina particles. The obtained metallographic sample with a mirror-like surface state was observed using a JEOL JSM7600F Scanning Electron Microscope (SEM) to be compared to earlier similar observations done on the initial alloy using another SEM (Philips XL30). The general or local chemical compositions were measured using the Energy Dispersion Spectrometry (EDS) device with which the JEOL SEM was equipped. The measurements of chemical compositions which will be performed are:

- the global chemical composition of the whole alloy (areas of about 0.2mm^2)
- the chemical composition of the matrix (pinpoint measurement)
- the global chemical composition of the re-melted/re-solidified zones (areas of about 1200μm^2)

Exploitation of the SEM micrographs by image analysis

Micrographs were acquired in the Back Scattered Electrons mode (BSE) with the JEOL SEM to be analyzed with the image analysis tool of the Photoshop CS software. What were of interest in a first time were the fractions of domains having obviously reached a molten state consecutively to the exposure to the very high temperature remaining to value. In order to get these areas in conditions allowing surface fraction measurements (more precisely without interactions with the other areas or particles existing in the not-melted parts of the alloy - grey matrix, white tantalum carbides - although that the re-solidification of the melted zones led to a finely structured poly-phase state displaying the similar grey levels), a "painting" in black under Photoshop was realized. The surface fractions which will be measured are:

- the cumulated surface fractions of the re-melted/re-solidified areas,
- the cumulated surface fractions of the TaC carbides mixed with the matrix in the not-remelted complementary areas.

Thermodynamic calculations

The calculated thermodynamic results, which are supposed to correspond to the previous metallographic results for one high temperature remaining to deduce, were obtained with the N-version of the Thermo-Calc software[6]. The later was used in association with a database built from the SSOL[7] one, which includes the descriptions of the Co-Cr-C system and its sub-systems[8-13] as well as systems involving the tungsten element (W). To allow representative calculations taking into account the possible presence of TaC carbides, the SSOL database was enriched with the descriptions of the binary and ternary sub-systems in which tantalum element is present: Ta-C, Co-Ta, Cr-Ta and Co-Ta-C[14-17].

RESULTS AND DISCUSSION

SEM examination of the initial and over-heated microstructures

Initially the microstructure of the piece was composed of (Figure 1):

- a dendritic matrix of cobalt containing a part of each of the other elements in solid solution,
- acicular chromium / tungsten carbides forming a eutectic compound with matrix is some interdendritic spaces,
- script-like tantalum carbides also forming a eutectic with the matrix in other interdendritic locations.

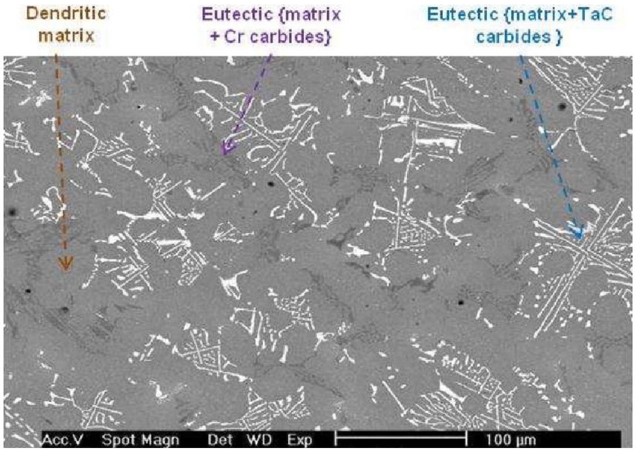

Figure 1 : Initial microstructure of the alloy (SEM, Back Scattered Electrons mode).

The new microstructure of the alloy after exposure to high temperature is illustrated in Figure 2.

The over-heating has obviously led to significant changes:

- there are compact or round areas of very fine microstructure, presenting seemingly the three phases chromium carbides, tantalum carbides and matrix together,
- the tantalum carbides are either fragmented into aligned compact white carbides (loss of their initial script-like shape), or they have become much coarser than at the origin (phenomenon probably resulting from the coalescence of many neighbor carbides together).

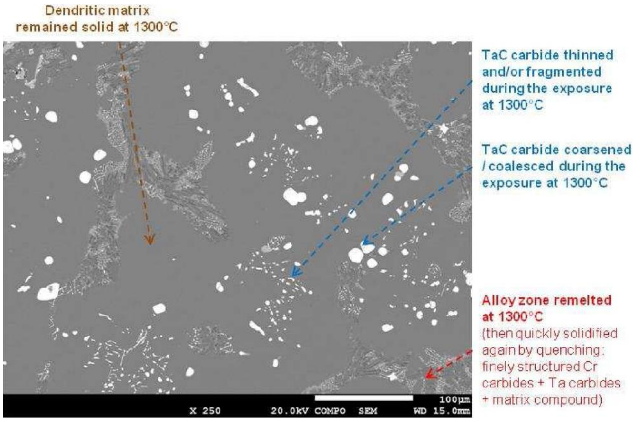

Figure 2 : Microstructure after quenching from the very high temperature (SEM, Back Scattered Electrons mode).

Results of the EDS analysis

First the global chemical composition of the alloy was controlled on the over-heated piece. This led to the average composition (over five different randomly selected areas) presented in TABLE 1. It appears that the initial chemical composition was globally kept, logically without any influence of the over-heating since the exposure was too short to induce catastrophic oxidation and then significant impoverishment in the most oxidable elements.

TABLE 1 : Average chemical composition as obtained from EDS measurements (five randomly selected areas); the carbon content, which cannot be measured by EDS, is assumed to be respected.

Main elements	Average value	Standard deviation
Co	Bal.	/
Ni	8.6	± 0.5
Cr	29.7	± 0.5
C	1.0 (targeted content)	/
Ta	6.5	± 0.8
W	6.4	± 0.2

As shown in Figure 3, the matrix presents almost the same chemical composition as the whole alloy. It contains all nickel, almost all chromium and all tungsten except the parts of both Cr and W involved in the dark carbides, but less than 1 wt.% of tantalum (because of an atomic ratio Ta / C lower than 1 the greatest part of the tantalum atoms are associated to carbon in the white TaC carbides).

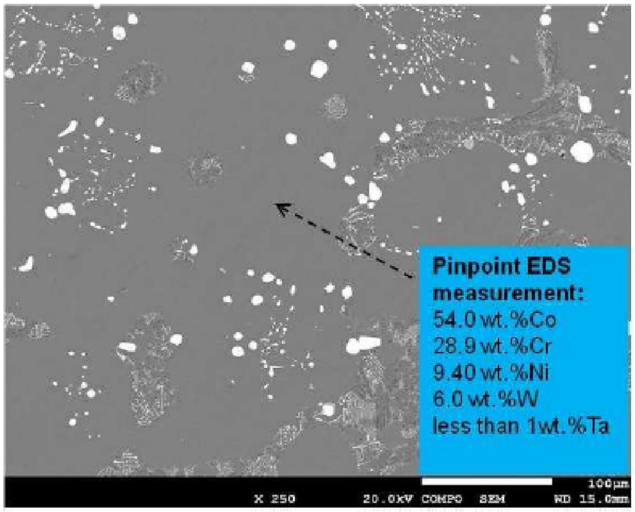

Figure 3 : Chemical composition of the matrix (SEM, Back Scattered Electrons mode).

The re-melted / re-solidified areas present chemical compositions sensibly different, as shown in TABLE 2. Indeed, they are poorer than matrix in nickel and richer in chromium and tungsten. At the exposure temperature the carbides still present were a part of the tantalum carbides (they have partially dissolved, their Ta and C atoms having integrated the matrix in solid solution) while the chromium & tungsten carbides were totally melted (less refractory eutectic). Due to the too rapid subsequent cooling, the Cr and W elements present in the liquid phase did not have time to diffuse in the neighbor solid areas, this resulting in such high concentrations.

TABLE 2 : Average chemical composition as obtained from EDS measurements (five areas taken in the re-melted / re-solidified zones); the carbon content, which cannot be measured by EDS, is assumed to be respected.

Main elements	Average value	Standard deviation
Co	Bal.	/
Ni	5.0	± 0.4
Cr	40.6	± 1.7
Ta	6.6	± 2.3
W	9.6	± 0.5

Results of the image analysis

Black masks were electronically drawn on the SEM micrographs over all the re-melted / re-solidified zones in order to clearly separate them from the other parts of the microstructures which were still solid at high temperature. This also allowed separating the fine white carbides appeared in these re-melted / re-solidified zones from the TaC carbides remaining among the still solid part of the alloy, this permitting to measure the surface fractions of the latter ones. An example of such masks is given in Figure 4.

The exploitation of these especially prepared electronic image files led to the surface fractions presented in TABLE 3. For the re-melted areas the corresponding mass fractions were assumed to be close to the surface or volume fractions since the volume masses of the still solid part and of the re-melted/re-solidified part of the alloy were supposed close to one another. In contrast, the corresponding values of mass fractions for the TaC carbides belonging to the still solid part of the alloy was calculated by taking 8.9 g/cm^3 for both the still solid part of alloy and its re-melted/re-solidified parts, and 14.5 g/cm^3 for the TaC carbides[18].

TABLE 3 : Surface fractions of the re-melted then re-solidified areas and of the TaC carbides belonging to the still solid part (and their corresponding mass fractions).

Re-melted / re-solidified zones	
Surface fractions from image analysis (surf.%)	
average	std deviation
16.03	3.74
TaC carbides in the still solid alloy	
Surface fractions from image analysis (surf.%)	
average	std deviation
2.62	0.54
Corresponding mass fractions (mass.%)	
average	std deviation
4.19	0.85

The possible values of the temperature of overheating

First propositions can be done for the real value of the exposure temperature by searching among the thermodynamic calculations results the temperatures which should lead to the chemical composition of the matrix as determined by EDS measurement. One can see in the first graph of Figure 5 that the temperature of 1262°C for which the calculated value of Ni content in the matrix is equal to the measured one (9.4 wt.% Ni), and the temperature of 1256°C for which the calculated value of the W content in the matrix is also equal to the measured one (6.0 wt.% W), can be proposed. In contrast, the calculated Ta content seems, whatever the temperature for calculation, in disagreement with the EDS experimental value (less than 1 wt.%Ta) but this is due to the fact that 1 wt.% is a limit of detection for the EDS technique. The real Ta content may be close to 1 wt.%.

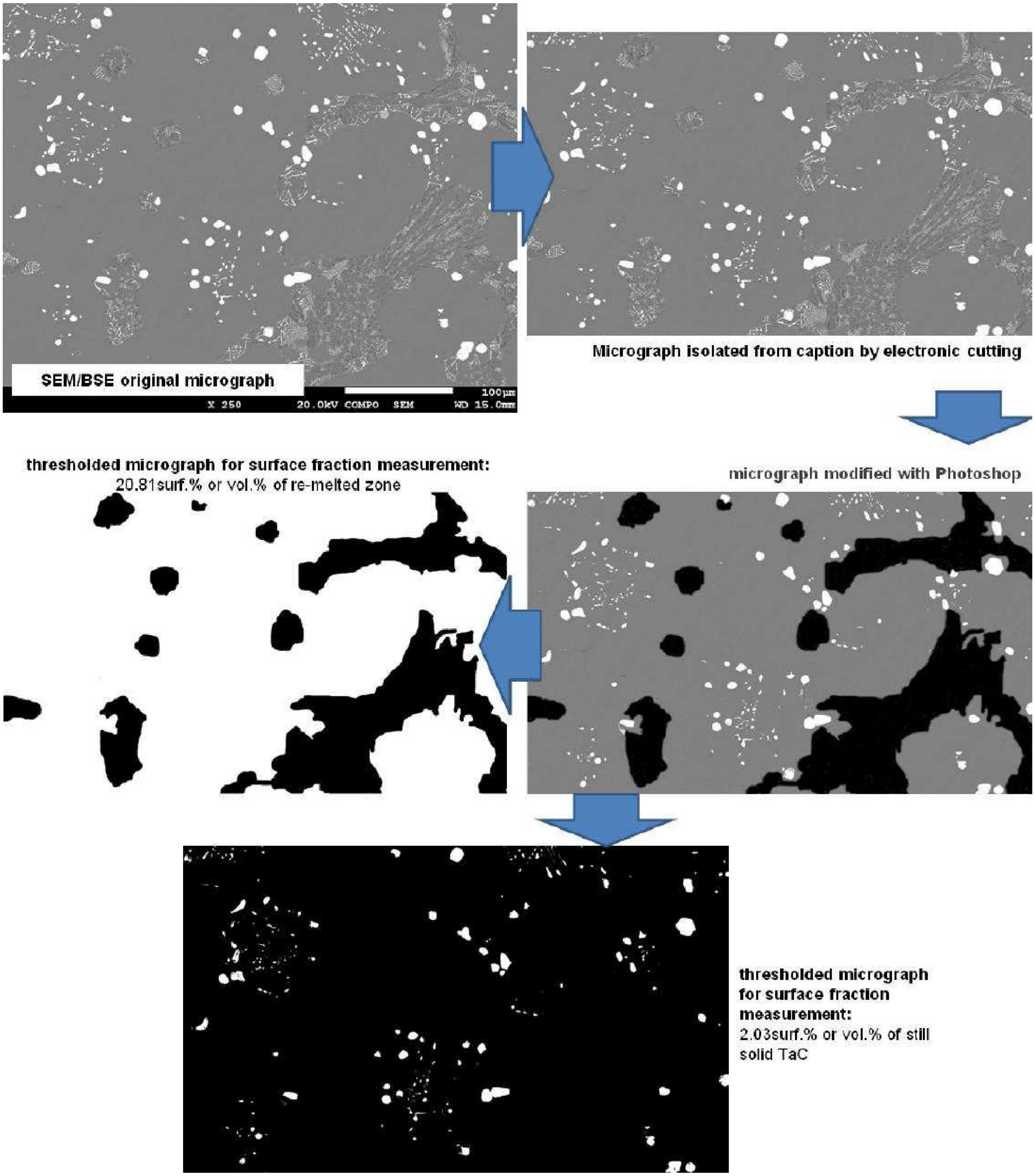

Figure 4 : The successive steps of micrograph preparation before image analysis (SEM, Back Scattered Electrons mode).

Additional propositions can be also done for this real exposure temperature by searching, using thermodynamic calculations, the temperatures which would lead to the values of the surface = volume = mass fraction of re-melted / re-solidified areas and to the solid-remained TaC carbides determined by image analysis on the SEM micrographs. Figure 6 shows that 1255°C and 1258°C well correspond to the surface or mass fraction of re-melted/solidified zone (16 surf.% ≈ 16 vol.% ≈ 16 mass.%) and to 4.19 mass.% of TaC, respectively. If the weight contents in Ni and in Cr were found by EDS in the molten/frozen zones as being respectively significantly lower and higher than what predicted by thermodynamic calculations, the tantalum and tungsten contents in these zones well correspond to the Thermo-Calc calculated ones for respectively 1260°C (6.69 wt.%Ta) and 1257°C (9.52wt.% W), as displayed in Figure 7. These values, which are consistent all together, give an average value of 1258°C.

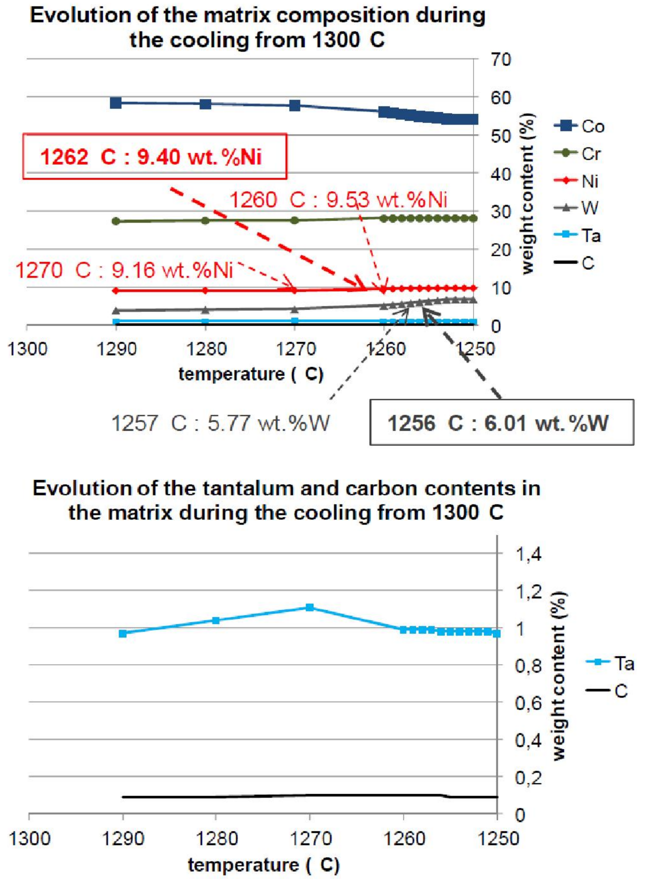

Figure 5: Chemical composition of the matrix at high temperature; identification of the temperatures corresponding to the Ni and W contents in matrix determined by EDS (Thermo-Calc calculations).

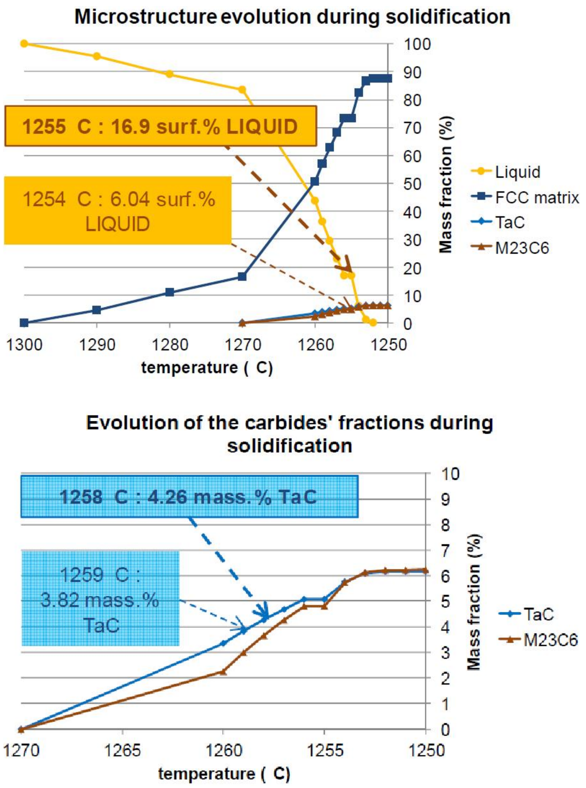

Figure 6 : Evolution of the nature and mass fractions of the different phases present versus temperature above 1250°C; identification of the temperatures corresponding to the Liquid and TaC mass fractions in the alloy determined by image analysis (Thermo-Calc calculations).

General commentaries

The cobalt-based alloy studied here was strongly reinforced by a very developed interdendritic network of carbides, among which a rather high fraction of tantalum carbides that are more refractory and stable at high temperature than the chromium/tungsten carbides. The significant population of eutectic carbides of the second type unfortunately decreased the refractoriness of the whole alloy and the temperature at which the piece was exposed was then higher than the alloy's solidus temperature marked by the re-melting of these carbides of chromium and tungsten, with consequently extended areas of liquid, the surface fractions of which were thus rather easy to value by image analysis. In contrast the eutectic tantalum carbides were not re-melted but the morphology of the TaC was significantly changed (fragmentation, coalescence, coarsening), another result of several hours spent at very high temperature.

This temperature, which can be qualitatively assessed in a first time as being comprised between the solidus temperature and the liquidus temperature (which can be also determined by thermodynamic calculations, or experimentally by Differential Thermal Analysis on a sample of alloy cut in the piece), was successfully much more precisely valued here by metallography ↔ calculations comparisons for several criteria: chemical compositions of matrix and of the frozen liquid, surface fraction of these frozen liquid zones and of the not re-melted TaC carbides.

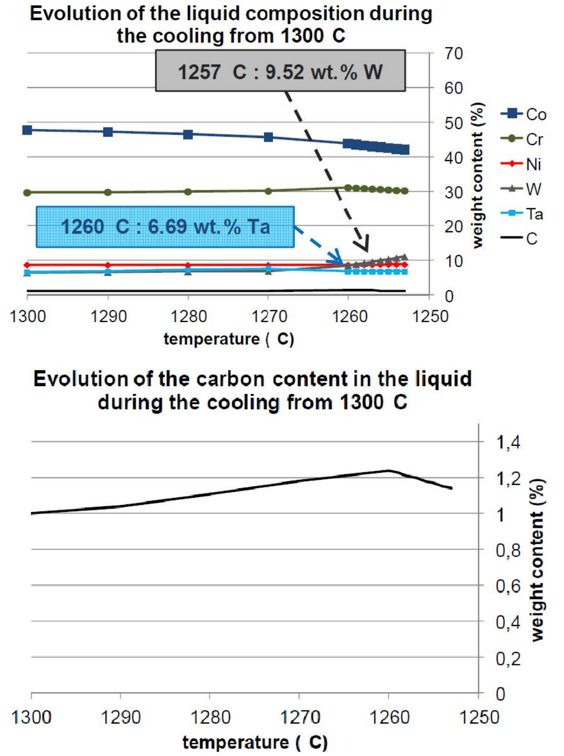

Figure 7 : Evolution of the chemical composition of the liquid phase at high temperature; identification of the temperatures corresponding to the Ta and W weight contents measured by EDS analysis in the frozen liquid (Thermo-Calc calculations).

CONCLUSIONS

Thus, the association of on one hand the metallographic results in terms of phase/compounds volume fractions and chemical compositions, and on the other hand the thermodynamic calculations, allowed in the case studied in this work identifying the temperature known by the piece partially molten because of a heating up to a temperature higher than the solidus one. The values obtained by four different ways are consistent, which lets think that the temperature finally determined is reliable. This demonstrates that thermodynamic calculations, further than a conception tool, can be also used as an expertise one, but at the condition of course that the used database is itself sufficiently reliable, as it was preliminary verified in the first part of this work.

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