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# Experimental and Thermodynamic Study of the Microstructure Evolution in Cobalt-base Superalloys at High Temperature

P. Berthod\*, S. Michon, L. Aranda, S. Mathieu, J.C. Gachon  
Laboratoire de Chimie du Solide Minéral (UMR 7555), Université Henri Poincaré  
BP 239, 54506 Vandoeuvre-lès-Nancy – France

\* Corresponding author's e-mail : [patrice.berthod@centraliens-lille.org](mailto:patrice.berthod@centraliens-lille.org)

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**Abstract.** Experiments and thermodynamic calculations were performed on five cobalt-base superalloys containing tantalum carbide and chromium carbides in order to evaluate the accuracy of thermodynamic calculation for this alloy family. The studied quantities were the solidus temperature and the phase fractions of the different carbides observed after a long time exposure at different high temperatures. The predicted and observed phases are in good agreement. However the measured phase-fractions and melting temperatures were sometimes higher than the calculated values. The disagreement in the phase fractions can be attributed to the fact that surface fractions and volume-fractions are not necessarily equal.

## Introduction

The properties of metallic alloys are governed by their microstructure, and the microstructure of superalloys can evolve during service at high temperature since the phases, their volume-fractions and morphology, present at room temperature generally differ from those that are stable at high temperature.

Thus, in order to employ metallic alloys at temperature as high as 1000 °C, the final microstructure, towards which the microstructure converges at the working temperature, must be taken into account. Therefore it is of great interest to predict the stable microstructure at high temperature from the chemical composition of a given superalloy. Moreover, if a better microstructure has been identified regarding the working conditions of the alloy, we have to determine the chemical composition that leads to the desired microstructure.

The calculations of thermodynamic equilibria are potentially very useful to find these chemical compositions. In this paper, the results of thermodynamic calculations for several compositions of superalloys were compared to the experimentally observed phases in alloys that were annealed at the same high temperatures and quenched. This work aims to evaluate the level of agreement between calculated predictions and experimental observations.

## Experimental Method

### Alloy Choice and Preparation

The composition and designation of the studied cobalt-base superalloys are listed in Table 1. The compositions were chosen so that the main elements are representative of cobalt-base superalloys that are used in the aeronautical industry or in industrial hot processes [1,2]. Compositions have been chosen to be simple enough to lead to the formation of a limited number of phases. Finally, large composition ranges were selected for the elements that have a notable effect on the microstructure. It should be kept in mind that:

- Nickel allows the stabilization of the face centered cubic structure of the cobalt matrix over a larger temperature range,

- Chromium gives to the alloys their high resistance against high temperature oxidation and corrosion by molten salts; in addition it participates in the formation of carbides,
- Carbon induces, in the case of foundry alloys, the formation of primary and secondary carbides, promoting good mechanical properties at high temperature such as creep resistance,
- Heavy metals, such as tungsten and/or tantalum, strengthen the alloys by forming a solid solution with cobalt as well as the formation of carbides.

Table 1 Compositions of the Studied Cobalt-Base Superalloys

	<b>Co</b>	<b>Ni</b> (wt.%)	<b>Cr</b> (wt.%)	<b>C</b> (wt.%)	<b>W</b> (wt.%)	<b>Ta</b> (wt.%)
<b>Co1</b>	bal.	8.6	28	0.22	5.8	3.0
<b>Co2</b>	bal.	8.7	28	0.37	/	5.8
<b>Co3</b>	bal.	8.9	29	0.49	/	8.5
<b>Co4</b>	bal.	8.5	29	0.38	5.8	3.0
<b>Co5</b>	bal.	8.9	29	0.98	/	5.8

The five superalloys were prepared under Argon gas from the pure elements (>99%, Alfa Aesar) using an induction furnace (Balzers, 20kg capacity). After melting, the alloys were kept for 15 min under intermittent electromagnetic stirring at approximately 1600 °C. The casting was performed in a sand mould bound by an Alphaset resin. The latter was placed in the furnace enclosure. The obtained pieces are cylindrical, with 25 mm diameter and 300 mm length.

The samples for the present study were taken from the bulk of the cast pieces. They are of compact shape with a volume of approximately 100 mm<sup>3</sup>. All of them were subjected to a homogenization treatment at 1200 °C for 2 hours, followed by a precipitation treatment at 1000 °C for 10 hours and finally air quenched.

### High Temperature Heat Treatment

In order to study the influence of the temperature on the microstructure, the five alloys, after the two-stage treatment, were each annealed for 5 hours at 1100 °C, 1200 °C and 1300 °C, respectively. These high temperature anneals were performed in a tubular Thermolyne 46200 furnace. The samples were then air quenched down to room temperature. Their initial microstructures after the precipitation treatment at 1000 °C were also examined.

The effect of three different heat treatment times was studied at 1300 °C. Samples of each alloy were treated as follows. In all cases, samples were heated from room temperature with a rate of 20 °C/min.

1. one sample was quenched in air at room temperature immediately after reaching 1300 °C,
2. one sample was kept for 5 hours at 1300 °C, then air quenched at room temperature,
3. one sample was kept for 20 hours at 1300 °C, then air quenched at room temperature.

### Surface Analysis

Samples were cut in two parts using an Accutom-2 saw equipped with a diamond blade. They were then embedded in a cold resin (Araldite CY230 +Strengthener Escil HY956). Polishing was done first with SiC paper from 80 to 1200 grid under water and finished with 6µm and 3µm diamond pastes. A Scanning Electron Microscope (SEM) was used in Back Scattered Electrons mode (BSE) under an acceleration voltage of 20kV. The phases present can be separated from one another since their average atomic numbers are significantly different. Spot microanalysis measurements allowed to clearly identify the present carbides. Surface fractions of the phases were determined using the AnalySIS software from Soft Imaging System GMBH.

### Thermal Analysis

Differential Scanning Calorimetric analysis was carried out for several alloys to determine their solidus temperature, which will be compared to the calculated ones. The heating rate was 20 °C/min up to 1200 °C, then 5 °C/min up to 1470 °C.

## Thermodynamic Modeling

Calculations were carried out for the chemical compositions of the superalloys, using the Thermo-Calc software [3]. The database used is SSOL (SGTE) [4], supplemented with descriptions of binary and ternary systems (Ta-C, Ta-Ni, Ta-Cr, Ta-Co, Co-Ta-C, Ni-Cr-Ta) [5 to 10]. The following quantities were of interest:

- the phases present at 1000 °C, 1100 °C, 1200 °C and 1300 °C,
- the molar or weight fraction of each phase present,
- the solidus temperature.

The weight fraction values obtained from Thermo-Calc were converted into volume fraction values according to the formula (1).  $f_{vol}(\phi_j)$ ,  $f_w(\phi_j)$  and  $\rho_j$  are the volume fraction, weight fraction and density of the phase  $\phi_j$ , respectively. The values used for the densities (expressed in  $\text{g.cm}^{-3}$ ) are 8.9 for matrix, 6.941 for  $\text{Cr}_7\text{C}_3$ , 6.953 for  $\text{Cr}_{23}\text{C}_6$  and 14.5 for TaC [11].

$$f_{vol}(\phi_j) = \left( \frac{f_w(\phi_j)}{\rho_{\phi_j}} \right) / \sum_i \left( \frac{f_w(\phi_i)}{\rho_{\phi_i}} \right) \quad (1)$$

## Experimental Results

### Initial Microstructure

Figure 1 and the first BSE image of Fig. 2 show the initial microstructures of the five cobalt-base superalloys after the two-stage treatment. The carbides present in grain boundaries are coarse primary carbides that formed during solidification. The two-stage heat treatment leads to the formation of thin precipitates of secondary carbides. In one of the alloys, the primary and secondary carbides are of the same phase type. The alloys Co1, Co2 and Co3 contain only one type of carbide according to their morphology and their average atomic number. According to chemical composition, the formula corresponds to MC carbides, here TaC. The alloy Co4 contains two types of carbides, the MC carbide and a carbide-matrix eutectic with a fine structure:  $\text{M}_{23}\text{C}_6$ . The MC carbide of this alloy is probably (Ta, W)C and  $\text{M}_{23}\text{C}_6$  is probably  $(\text{Cr,W})_{23}\text{C}_6$ . The alloy Co5 also contains two types of carbides, eutectic TaC and eutectic  $\text{M}_7\text{C}_3$ .

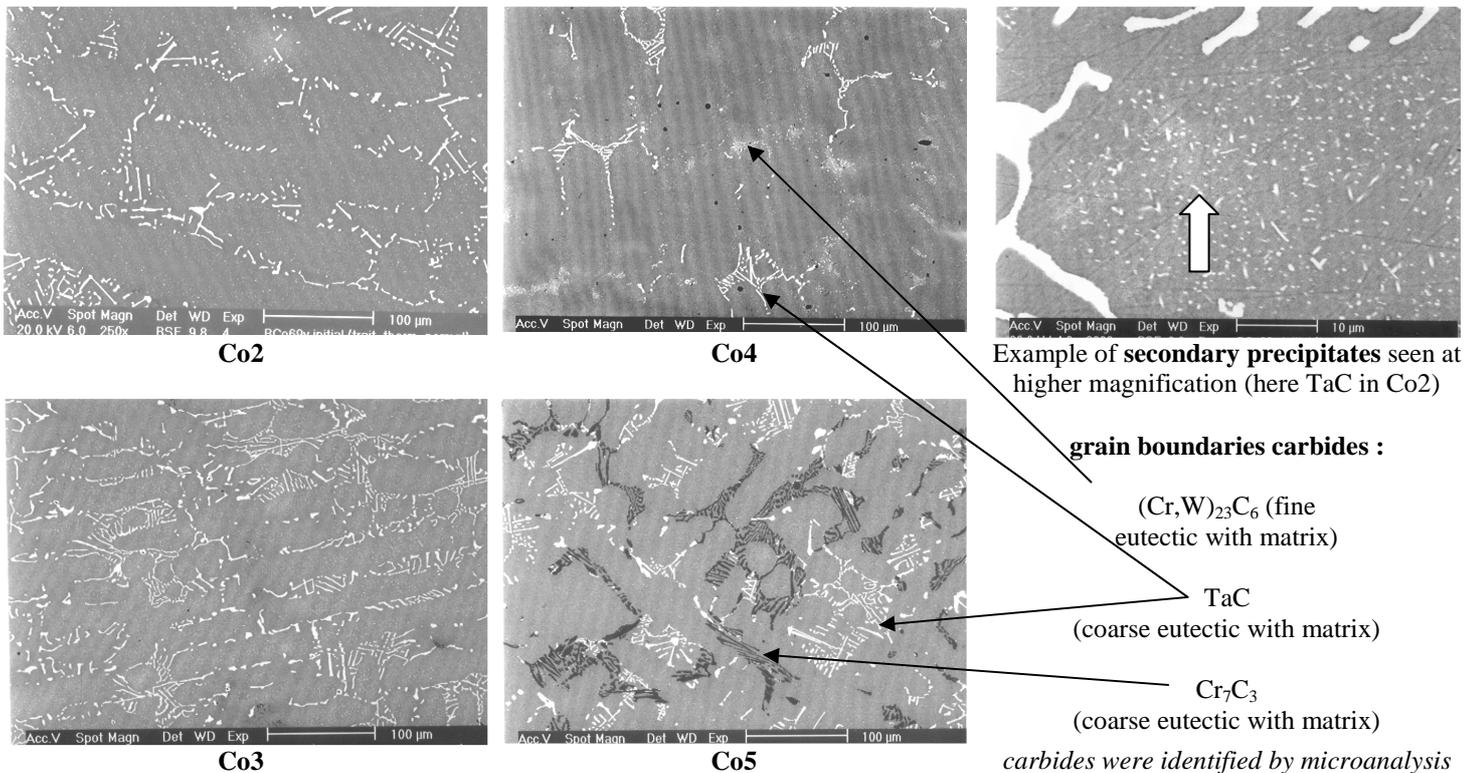


Figure 1 Initial microstructures of four cobalt-base superalloys (BSE images)

### Microstructure after 5 hours at High Temperature

The BSE images of the Co1 alloy after the 5 hours at 1100, 1200 and 1300°C are shown in Fig. 2. The amount of secondary carbides decreases with increasing temperature until they are finally dissolved (not visible in Fig.2 because of the too low magnification). The primary carbide was dissolved after the 1300 °C/5 h heat treatment. No partial melting was observed for all the alloys up to 1200 °C, whereas at 1300 °C Co4 and Co5 showed molten zones located at grain boundaries. These are alloys containing initially two types of eutectic carbides. As it can be seen on Fig. 3, it seems that the molten zones correspond to the <matrix-chromium carbide> eutectic.

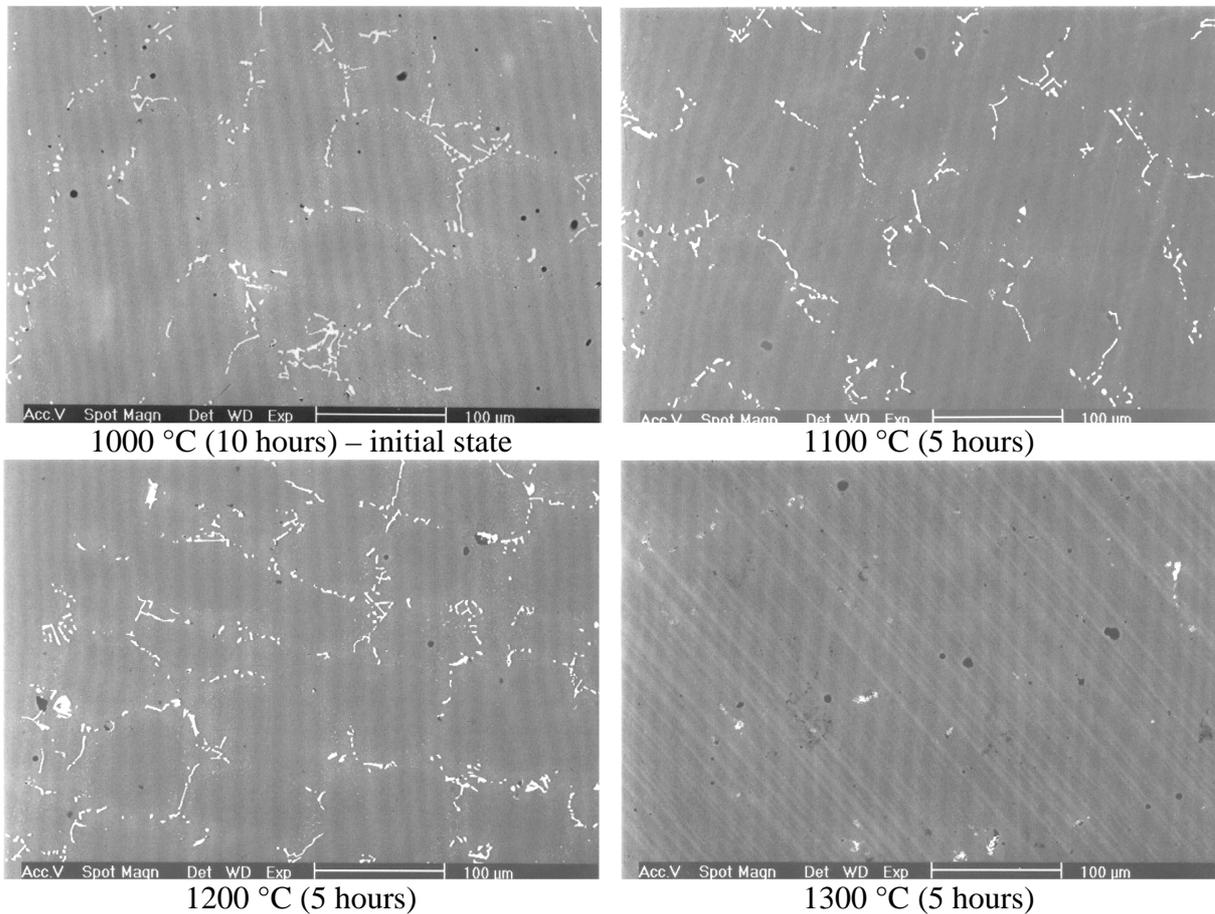


Figure 2 Co1 microstructures after heat treatment at different temperatures (BSE images)

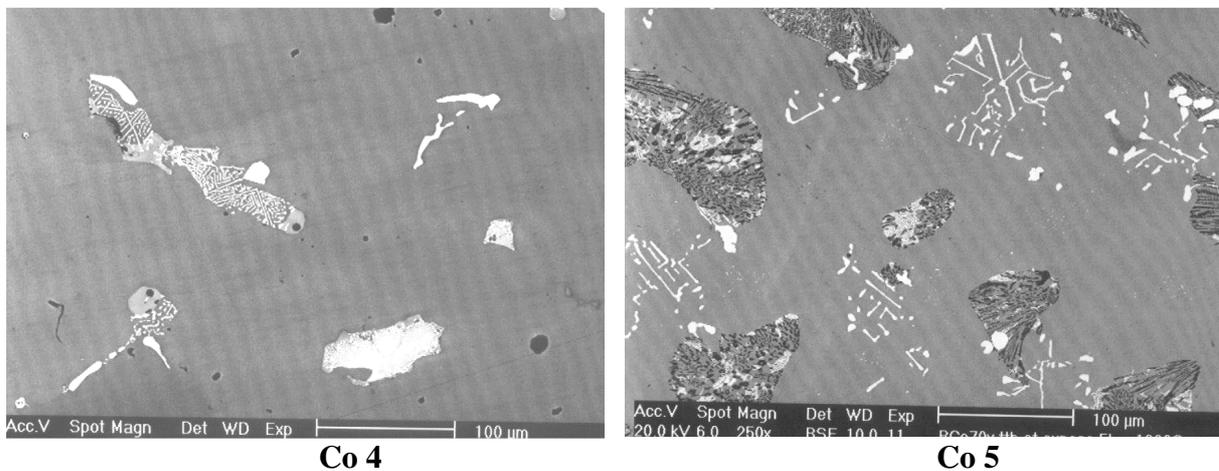


Figure 3 Co4 and Co5 microstructures after 5 hours at 1300 °C (BSE images)

These different eutectic zones are easily distinguishable. The local microstructure resulting from the new solidification is much finer than elsewhere in the alloy. This is due to the high speed of cooling (air quenching). Since only the chromium carbides are observed in these domains, we suggest that the <matrix-chromium carbide> eutectic is molten at 1300 °C. The <matrix-MC carbide> eutectic remains solid at this temperature.

### Microstructure versus Annealing Time

Alloys Co1 to Co3 do not show molten zones after annealing for 5 hours at 1300 °C. In order to assess the stability with time, longer anneals were performed (20 hours). Different behaviors were observed for the three alloys. For example the microstructure of Co1 evolves rapidly. The alloy already contains a low carbide fraction after reaching 1300 °C and, after annealing for 5 hours, carbides are no longer present (Fig.2). Contrarily, the microstructure of Co3 remains unchanged independent of annealing time (Fig.4).

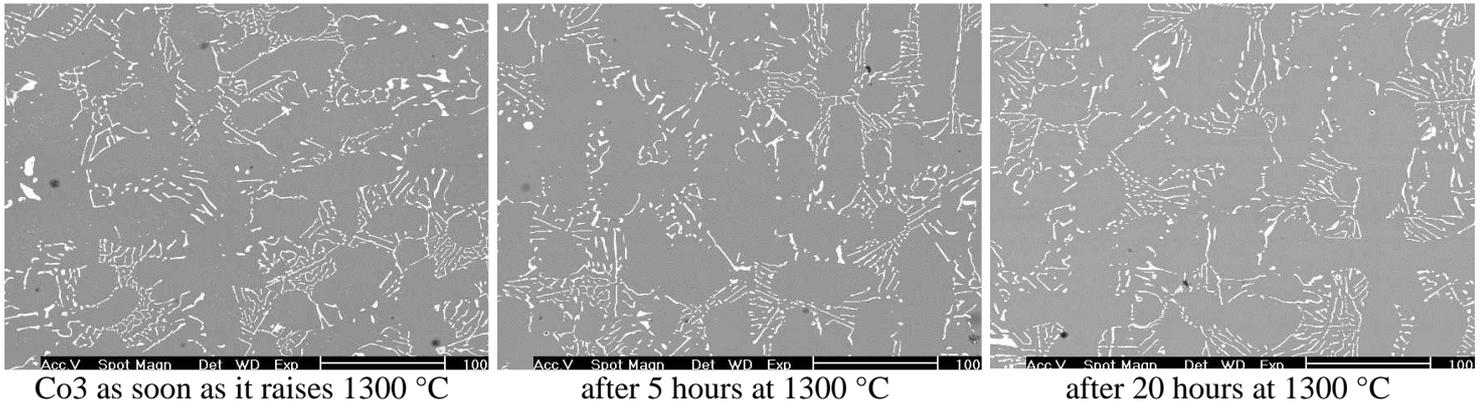


Figure 4 Microstructure evolution as a function of time of Co3 at 1300 °C (BSE images)

### Surface-Fraction Analysis

For a quantitative analysis, the surface fraction of each phase was determined by image analysis. The results are listed in Tables 2 and 3 (the experimental uncertainty is of about +/- 0.5%<sub>surf</sub>). It can be seen in Table 2 that, with increasing temperature, the carbide surface-fraction decreases of alloys Co1, Co2 and Co3, which have only the MC carbide.

However, no change is observed if the alloy contains two types of carbides (Co4 and Co5). Table 3 shows that there is no change in carbide surface-fraction at 1300 °C with increasing annealing time for alloys Co2 and Co3 whereas for Co1 all the carbides are rapidly dissolved.

Table 2 Surface Fraction of the Phases Annealed for 5 Hours at Different Temperatures

	Co1	Co2	Co3	Co4	Co5
<b>1300 °C</b>	0.2 % MC	2.4 % MC	6.7 % MC	? % MC partial melting	? % MC partial melting
<b>1200 °C</b>	2.2 % MC	5.4 % MC	7.5 % MC	2.9 % MC ? % M <sub>23</sub> C <sub>6</sub>	4.9 % MC 5.8 % M <sub>7</sub> C <sub>3</sub>
<b>1100 °C</b>	1.9 % MC	7.1 % MC	10 % MC	2.4 % MC ? % M <sub>23</sub> C <sub>6</sub>	5.2 % MC 5.3 % M <sub>7</sub> C <sub>3</sub>
<b>1000 °C</b>	2.4 % MC	4.8 % MC	8.9 % MC	2.5 % MC ? % M <sub>23</sub> C <sub>6</sub>	5.6 % MC 5.3 % M <sub>7</sub> C <sub>3</sub>

Table 3 Surface Fraction of the Phases Annealed at 1300 °C for Different Times

	Co1	Co2	Co3
<b>Just reaching 1300 °C</b>	0.8 % MC	4.0 % MC	7.6 % MC
<b>5 hours at 1300 °C</b> (values table 2)	0.1 % MC (0.2 % MC)	4.0 % MC (2.4 % MC)	6.7 % MC (6.7 % MC)
<b>20 hours at 1300 °C</b>	not studied	3.9 % MC	6.9 % MC

### Thermal Analysis

Thermal analyses were performed for alloys Co2 to Co5 by Differential Scanning Calorimetry (DSC). The curves obtained for alloy Co3 are shown as an example in Fig. 5. Two endothermic peaks are observed. They correspond to the melting of the <matrix-MC carbide> eutectic (beginning at approximately 1320 °C) and the melting of the matrix (end at approximately 1384 °C), respectively. The derived temperatures are listed in Table 4. The solidus temperatures of the alloys are around 1300 °C. The solidus temperature of the alloy richest in refractory metals (Co3) is approximately 30 °C higher than that of the other alloys.

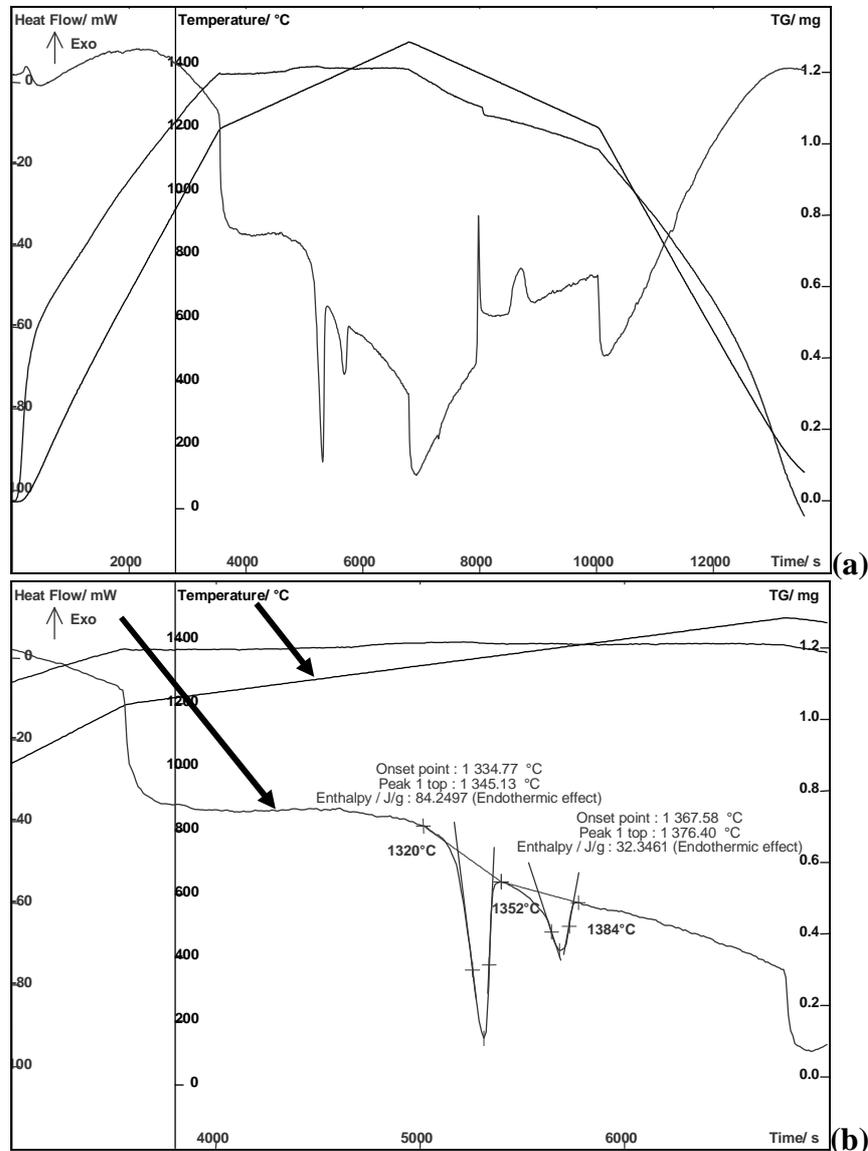


Figure 5 DSC curves of Co3 (a), magnification of the heating curve (b).

Table 4 Solidus Temperatures for Co2 to Co5 derived from Thermal Analysis

	Co2	Co3	Co4	Co5
$T_{\text{solidus}}$	1290 °C	1320 °C	1288 °C	1291 °C

### Results from Thermodynamic Calculations

Phase equilibria calculations were carried out to predict the microstructural evolution of these alloys. The results are listed in Table 5.

The calculated results show that all alloys, except for Co3, contain two types of carbides at 1000 °C: MC and  $M_{23}C_6$ . However, the amount of  $M_{23}C_6$  is only significant in the Co4 and Co5 alloys. The fraction of the carbides decreases with increasing temperature. With increasing temperature  $M_{23}C_6$  dissolves in alloy Co2 between 1000°C and 1100°C, while  $M_7C_3$  forms in alloy Co5. All alloys are partly molten at 1300°C.

Table 5 Calculated Weight Fractions of the Equilibrium Phases at Different Temperatures.

weight %	Co1		Co2		Co3		Co4		Co5	
<b>1300 °C</b>	Matrix	70.9 %	Matrix	58.7 %	Matrix	35.5 %	Matrix	58.4 %	Matrix	28.5 %
	Liquid	0.02 %	Liquid	41.3 %	Liquid	64.5 %	Liquid	41.6 %	Liquid	71.5 %
<b>1200 °C</b>	Matrix	97.6 %	Matrix	95.0 %	Matrix	92.6 %	Matrix	94.7 %	Matrix	88.4 %
	MC	2.40 %	MC	5.02 %	MC	7.36 %	MC	2.43 %	MC	5.38 %
	$M_{23}C_6$	0.78 %					$M_{23}C_6$	2.90 %	$M_7C_3$	6.18 %
<b>1100 °C</b>	Matrix	97.0 %	Matrix	94.7 %	Matrix	92.4 %	Matrix	94.1 %	Matrix	88.0 %
	MC	2.49 %	MC	5.34 %	MC	7.61 %	MC	2.51 %	MC	5.53 %
	$M_{23}C_6$	0.52 %					$M_{23}C_6$	3.41 %	$M_7C_3$	6.48 %
<b>1000 °C</b>	Matrix	96.7 %	Matrix	94.4 %	Matrix	92.2 %	Matrix	93.7 %	Matrix	83.6 %
	MC	2.57 %	MC	5.54 %	MC	7.77 %	MC	2.58 %	MC	5.63 %
	$M_{23}C_6$	0.78 %	$M_{23}C_6$	0.07 %			$M_{23}C_6$	3.67 %	$M_{23}C_6$	10.7 %

Note: Matrix = fcc-Co solid solution

The volume fractions derived from  $f_{\text{vol}}(\varphi_j) = \frac{f_w(\varphi_j)}{\rho_{\varphi_j}} / \sum_i \left( \frac{f_w(\varphi_i)}{\rho_{\varphi_i}} \right)$  are listed in Table 6. The solidus

temperatures determined by Thermo-Calc from the thermodynamic database for each alloy are given in the first line of the table.

Table 6 Volume Fractions of the Phases calculated from the Weight Fractions given by Thermo-Calc

	Co1		Co2		Co3		Co4		Co5	
$T_{\text{solidus}}$ °C	1257		1287		1277		1253		1277	
<b>1200 °C</b>	MC	1.49 %	MC	3.14 %	MC	4.65 %	MC	1.49 %	MC	3.31 %
	$M_{23}C_6$	0.03 %					$M_{23}C_6$	3.72 %	$M_7C_3$	7.95 %
<b>1100 °C</b>	MC	1.54 %	MC	3.35 %	MC	4.81 %	MC	1.54 %	MC	3.40 %
	$M_{23}C_6$	0.67 %					$M_{23}C_6$	4.37 %	$M_7C_3$	8.33 %
<b>1000 °C</b>	MC	1.59 %	MC	3.47 %	MC	4.92 %	MC	1.58 %	MC	3.43 %
	$M_{23}C_6$	1.01 %	$M_{23}C_6$	0.10 %			$M_{23}C_6$	4.70 %	$M_{23}C_6$	13.6 %

## Discussion: Comparison between Experimental and Calculated Results

The Table 7 shows both experimental and calculated results for the 5 alloys at temperatures where the alloys are undoubtedly 100 % solid.

Generally good agreement is observed between experiment and calculation in terms of the phase types, except for Co1 and Co2. The MC eutectic carbides were always detected in the microstructure, whereas the chromium carbides were only observed when their volume fraction was sufficient.

The calculation shows that the phase-fractions of MC and the chromium carbides, if present, decrease systematically with increasing temperature. The same general trend was observed in the microstructures.

Table 7 Comparison of Surface Fractions of the Phases determined from the Microstructures and Volume Fractions obtained from Thermo-Calc.

temperature	Co1		Co2		Co3		Co4		Co5	
	exp. % <sub>surf</sub>	calc. % <sub>vol</sub>								
1200 °C										
MC	2.2	1.49	5.4	3.14	7.5	4.65	2.9	1.49	4.9	3.31
M <sub>7</sub> C <sub>3</sub>	/	/	/	/	/	/	?	/	5.8	7.95
M <sub>23</sub> C <sub>6</sub>	/	0.03	/	/	/	/	?	3.72	/	/
1100 °C										
MC	1.9	1.54	7.1	3.35	10	4.81	2.4	1.54	5.2	3.40
M <sub>7</sub> C <sub>3</sub>	/	/	/	/	/	/	?	/	5.3	8.33
M <sub>23</sub> C <sub>6</sub>	/	0.67	/	/	/	/	?	4.37	/	/
1000 °C										
MC	2.4	1.59	4.8	3.47	8.9	4.92	2.5	1.58	5.6	3.43
M <sub>7</sub> C <sub>3</sub>	/	/	/	/	/	/	?	/	/	/
M <sub>23</sub> C <sub>6</sub>	/	1.01	/	0.10	/	/	?	4.70	5.3	13.6

The surface fractions of the phases are generally different from the volume fractions determined by  $f_{vol}(\varphi_j) = \frac{f_w(\varphi_j)}{\rho_{\varphi_j}} / \sum_i \left( \frac{f_w(\varphi_i)}{\rho_{\varphi_i}} \right)$  from the weight fractions given by Thermo-Calc. These differences cannot be always explained by the experimental uncertainty of surface-fraction measure. Firstly it can be thought that they may be due to the fact that the alloys did not reach full equilibrium experimentally (annealing for 5 hours at high temperature could have been too short). However, the preliminary homogenization treatment and the stability of the structures annealed for 20 hours at 1300 °C for two of the three alloys (Co1 being an exception) do not support the non-equilibrium assumption. The fact that experimental surface fractions are larger than the calculated ones is likely due to other factors than non-equilibrium. Indeed, it is probably unsuitable to directly compare surface fractions and volume fractions, because of the complex shape of these eutectic carbides.

The evaluation of relations between surface fraction values and volume fraction values, such as for spherical particles (Saltykov's algorithm) was outside the scope of the present work. The attempt was made to derive a proportional relation between the two sets of values. Table 8 shows the values of the ratio surface fraction / volume fraction. When possible this evaluation was carried out for the all the phases within one sample. The ratio is generally close to 1.6 (average value 1.645) for the MC carbides, i.e. for 10 of 15 alloys that were analyzed. The values of the remaining alloys are not very different from 1.6. For the M<sub>7</sub>C<sub>3</sub> carbides, the average ratio is 0.6 but with more scatter in the values.

The experimental melting temperatures and the calculated solidus temperatures are less in agreement (Table 9). Indeed, the calculation predicts for all alloys that the melting should begin at 1300 °C but this was experimentally observed only for two of the five alloys. It should be noted that the experimental observed microstructure after exposure at 1300°C and thermal analysis result are not always consistent. For example, the microstructure of alloy Co2 did not show any melting after exposure at 1300 °C, while the thermal analysis

shows a solidus temperature 10 °C below 1300 °C. However, the other alloys showed good agreement between the results from thermal analysis and their microstructure after exposure at 1300 °C.

phase		Ratio $f_{\text{surf}} \phi_j / f_{\text{vol}} \phi_j$				
		Co1	Co2	Co3	Co4	Co5
1200 °C	MC	1.48	1.72	1.61	1.95	1.48
	M <sub>7</sub> C <sub>3</sub>					0.73
1100 °C	MC	1.23	2.12	2.08	1.56	1.53
	M <sub>7</sub> C <sub>3</sub>					0.64
1000 °C	MC	1.51	1.38	1.81	1.58	1.63
	M <sub>23</sub> C <sub>6</sub>					0.39

Table 9 Comparison between the Experimental and Calculated Results at 1300 °C, and between the Solidus Temperatures derived from DSC and those predicted from the Calculation.

	Co1		Co2		Co3		Co4		Co5	
	exp.	calc.								
<b>melting at 1300°C?</b>	No		No		No		Yes		Yes	
		Yes								
		1257		1287		1277		1253		1277
<b>T<sub>solidus</sub> (°C)</b>	/		1290		1320		1288		1291	

## Conclusion

For the microstructure evolution of superalloys, good agreement was obtained between experimental results and those determined by thermodynamic calculation. However, there is quantitative disagreement between the results. Although experiment and calculation show the same trend, the experimental surface fractions (measured on samples) and the volume fractions (obtained from the calculated weight fractions) are noticeably different. But it is also possible that the relation between a surface fractions and a corresponding volume fraction is not as simple as an equality and this fact can explain the differences observed. Indeed a constant ratio was found to convert surface fraction values of MC carbides to volume fractions. This allowed to compare the experimental and calculated values. The temperatures corresponding to the beginning of melting between experiment and calculation do not agree well, but the differences appears to be acceptable considering that the database is not yet completed.

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