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INTRODUCTION

High temperature properties of superalloys more depends on their microstructure than their chemical composition. It's especially true for cast cobalt-based alloys: several characteristics of the interdendritic carbides network govern their mechanical resistance. Quantities, morphologies and natures of carbides do not remain like they were just after solidification or heat treatment when exposed to high temperature for a long time. Indeed, they are evolving to reach the thermodynamically stable state corresponding to the considered temperature. Thermodynamical calculations are very useful to know the final microstructure the alloys are converging to, or to target the chemical compositions leading to thermodynamically-stable microstructures suitable to the wanted properties.

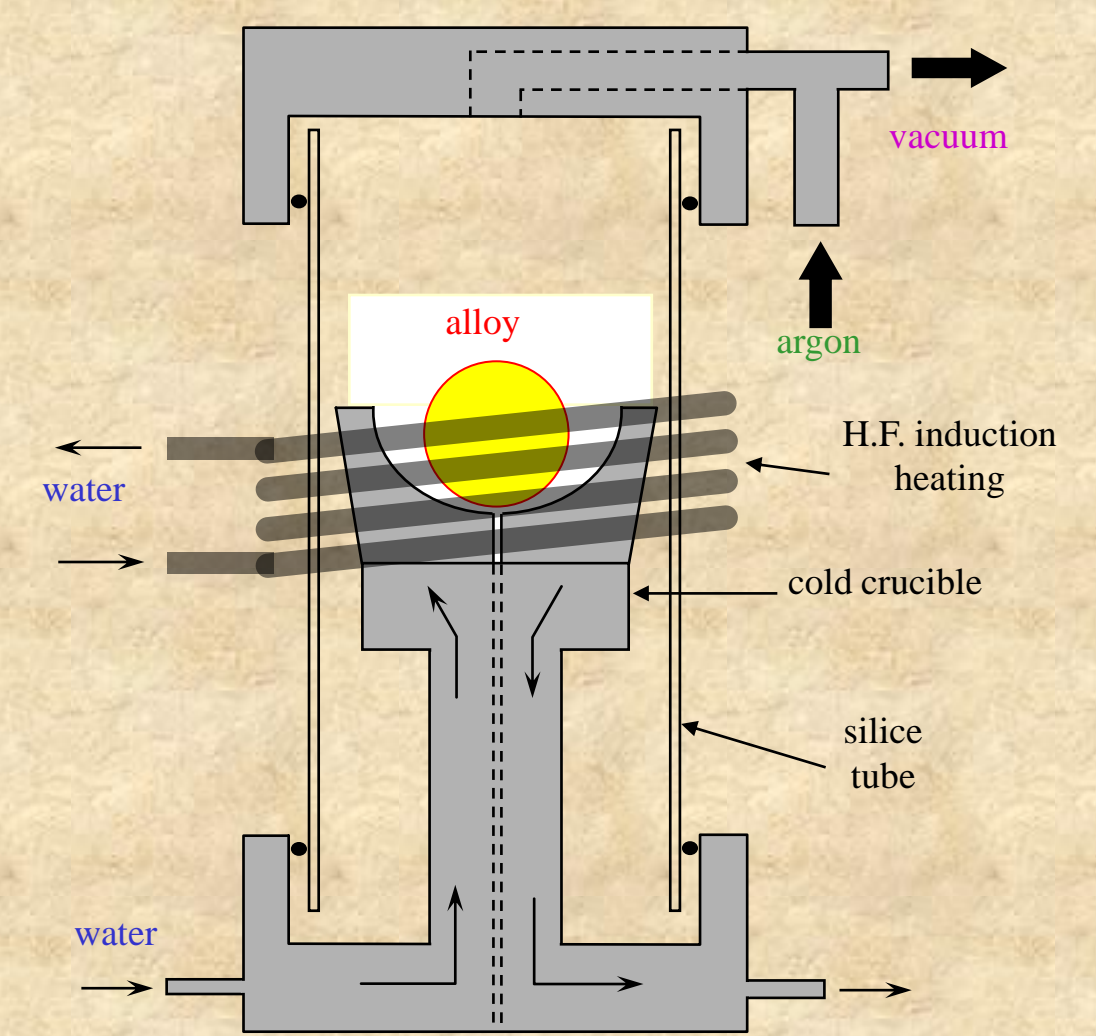
The agreement between predicted stable metallurgical states and real microstructures was assessed. For this purpose, the natures and quantities of the different phases of several selected alloys held few hours at high temperatures were compared to those calculated by Thermo-Calc.

CHARACTERISTICS OF THE STUDIED ALLOYS

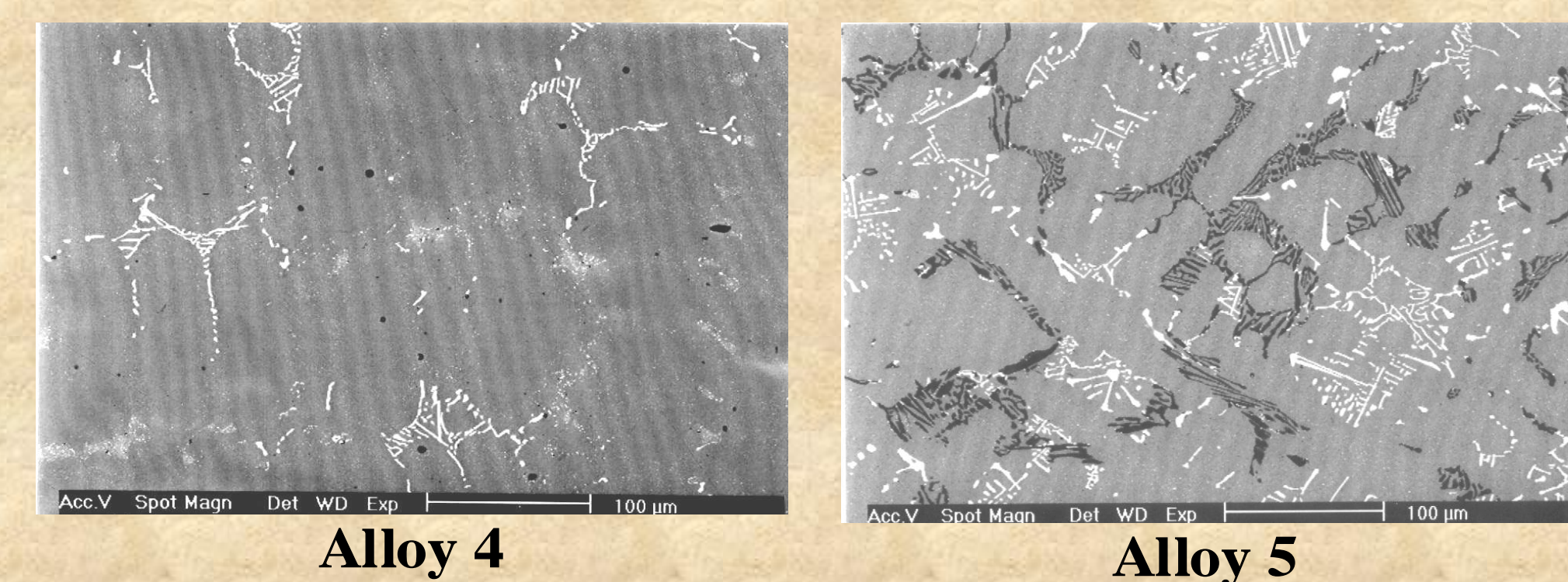
Five different alloys were prepared by high frequency induction melting in a cold crucible and under argon gas, then heat treated in two stages :

- homogenized 2h at 1200°C,
- aged 10h at 1000°C, and air quenched.

Their compositions were chosen in order to represent a large panel of cobalt-base superalloys strengthened by carbides. Nickel and chromium contents are equals for all the alloys, but different carbon and tantalum contents were selected.

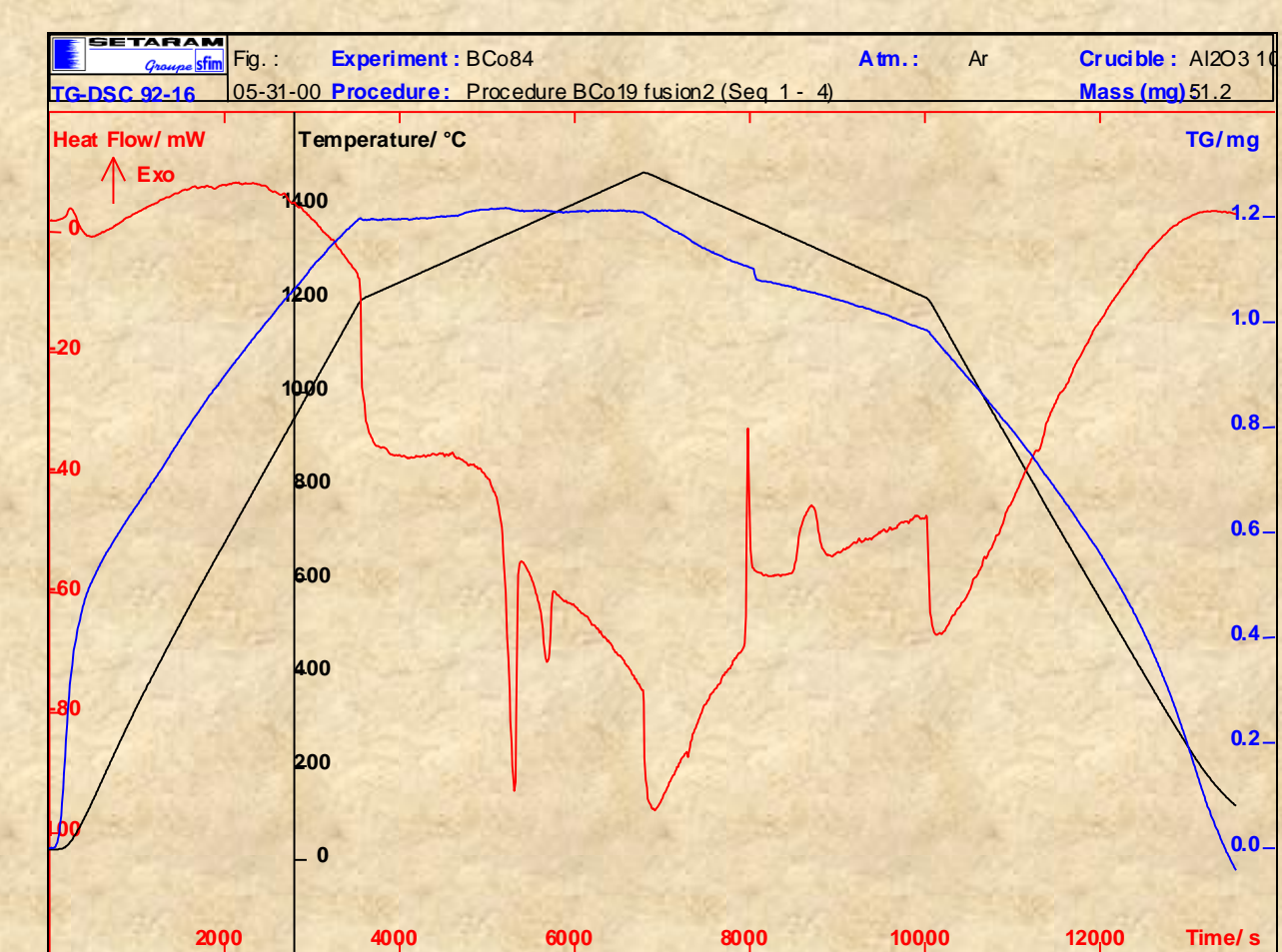


Chemical Composition (weight percent)	Co	Ni	Cr	C	W	Ta
Alloy 1	bal.	8.6	28	0.22	5.8	3.0
Alloy 2	bal.	8.7	28	0.37	/	5.8
Alloy 3	bal.	8.9	29	0.49	/	8.5
Alloy 4	bal.	8.5	29	0.38	5.8	3.0
Alloy 5	bal.	8.9	29	0.98	/	5.8

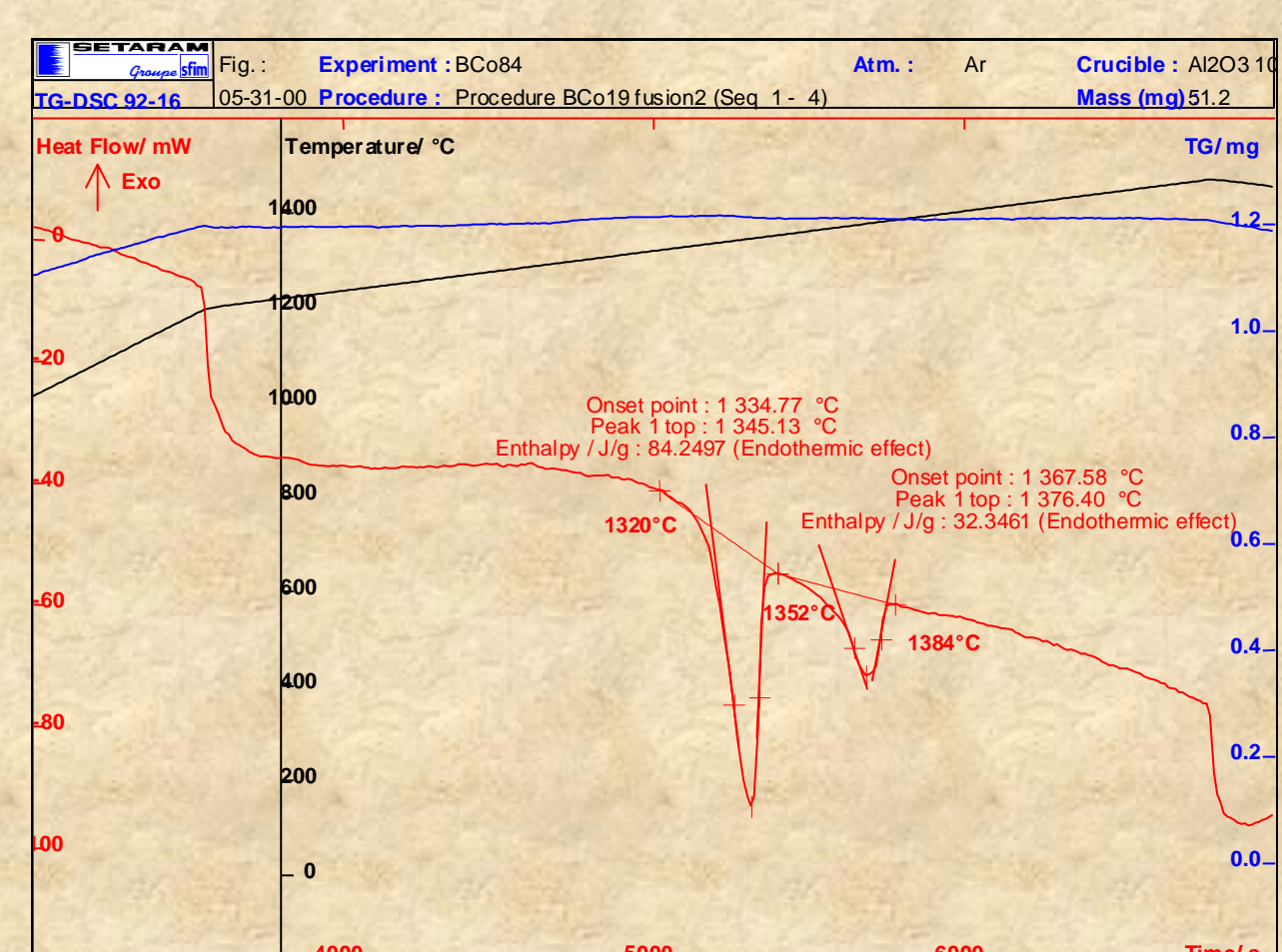


The obtained microstructures exhibit different carbides types and densities. Tantalum carbides (TaC), and/or chromium carbides such as Cr₇C₃ or (Cr,W)₂₃C₆, are present at grain boundaries. Their density is governed by the carbon content.

COMPARISON CALCULATIONS <-> EXPERIENCES



	Alloy 2	Alloy 3	Alloy 4	Alloy 5
T _{solidus} from DTA Heating	1288°C	1284°C	1288°C	1281°C
T _{solidus} from DTA Cooling	1263°C	1249°C	1250°C	1270°C
T _{solidus} from TC calculation	1287°C	1277°C	1253°C	1277°C

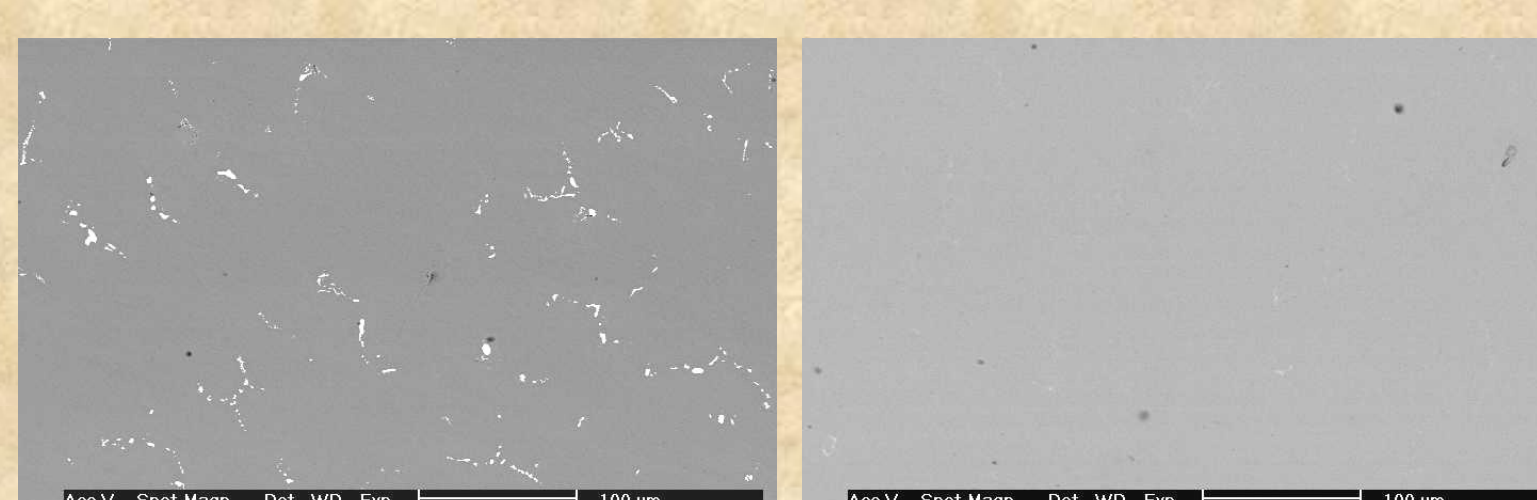


Experimental results consisted first in a determination of solidus temperatures by Differential Thermal Analysis (DTA), then compared to those issued from Thermo-Calc N version using a completed SSOL database.

The calculated solidus values are all located in the interval: [T_h, T_c] where T_h is the temperature obtained during heating and T_c during cooling].

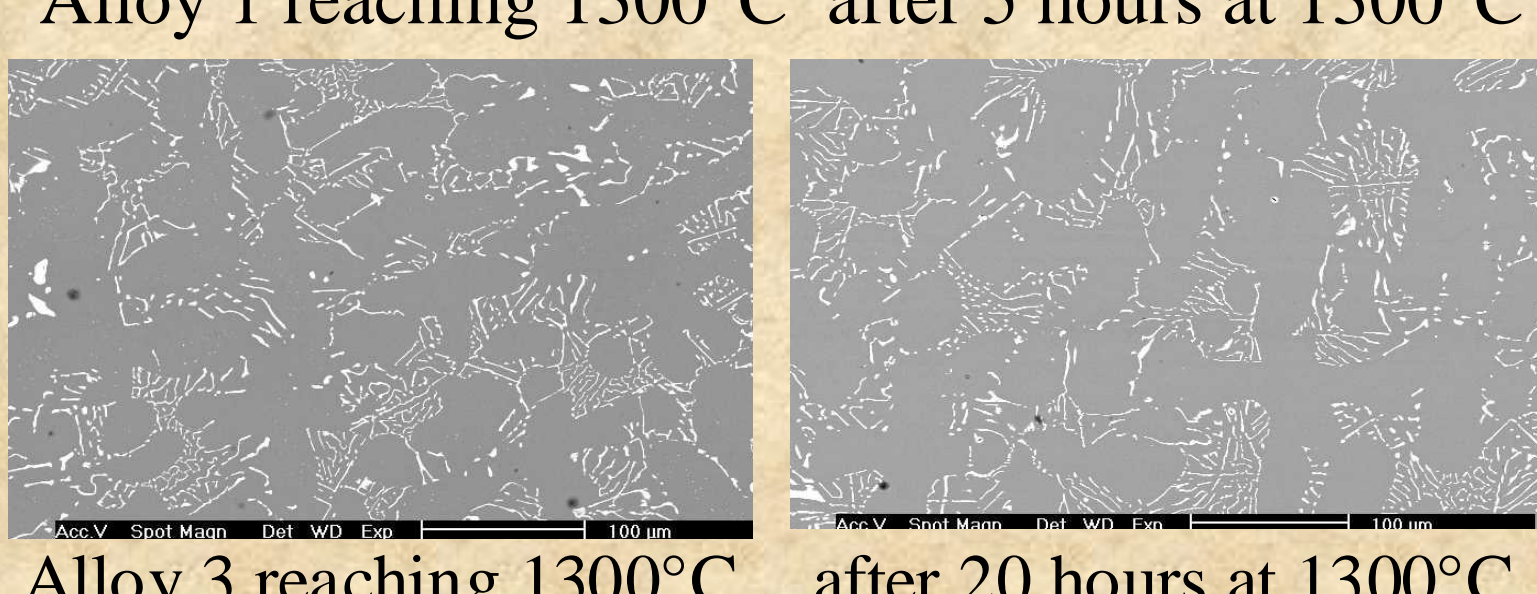
For the comparisons with the microstructural Thermo-Calc predictions, the alloys were exposed in a muffle furnace at several high temperatures, then quenched by air cooling. Different heat treatment durations were applied to the alloys to be closed to the stable microstructural state: five hours appeared sufficient.

Alloys followed different evolutions. For example, at 1300°C, Alloy 1 lost all its MC carbides. At the opposite, MC network remained stationary for the Alloy 3.

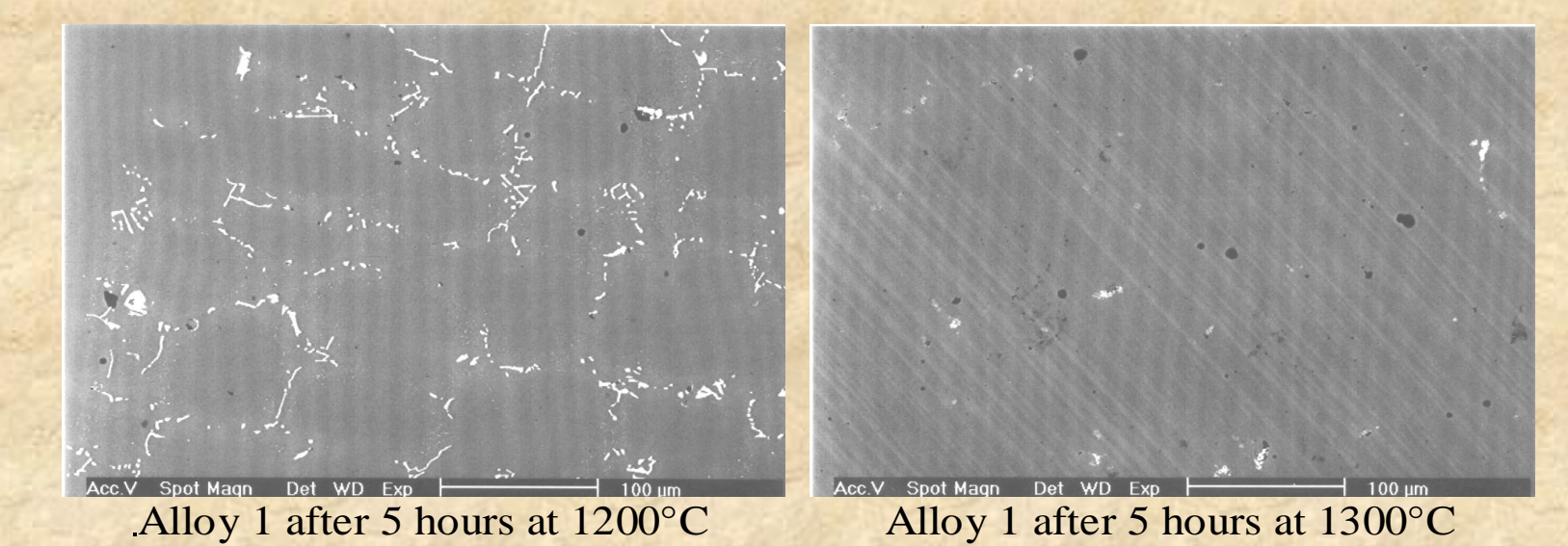
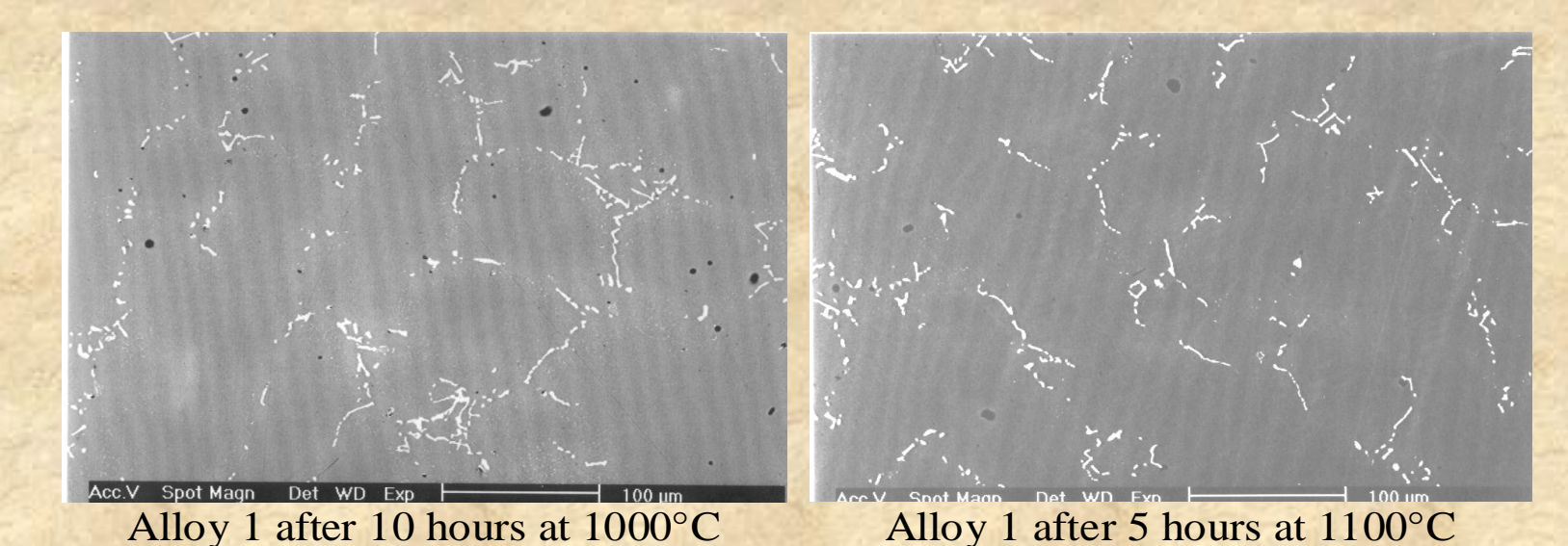


Surprisingly no beginning of fusion was evidenced at this temperature, despite of the measured or calculated solidus value.

carbides' area fractions	Alloy 1	Alloy 2	Alloy 3
reaching 1300°C	0.8% MC	4.0% MC	7.6% MC
5 hours at 1300°C	0.1% MC	4.0% MC	6.7% MC
20 hours at 1300°C	/	3.9% MC	6.9% MC



Except for 1000°C, which corresponds to the ageing treatment applied initially, all the alloys were exposed during 5 hours to high temperature, then air quenched. It appears that the higher the temperature, the lower the area fraction of each type of carbides. Moreover, for Alloy 5, a change of the nature of chromium carbides takes place at 1100°C and above.



Thermo-Calc calculations were made for all the alloys and three different temperatures. Usually, the mass fraction (or volumic fraction obtained with the following formula) of each type of carbide decreased with temperature, as it can also be seen on alloys.

carbides' area fractions	Alloy 1		Alloy 2		Alloy 3		Alloy 4		Alloy 5	
	exp. (% _{surf})	calc. (% _{vol})	exp. (% _{surf})	calc. (% _{vol})	exp. (% _{surf})	calc. (% _{vol})	exp. (% _{surf})	calc. (% _{vol})	exp. (% _{surf})	calc. (% _{vol})
1200°C										
MC	2.2	1.49	5.4	3.14	7.5	4.65	2.9	1.49	4.9	3.31
M ₇ C ₃	/	/	/	/	/	/	/	/	5.8	7.95
M ₂₃ C ₆	/	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 ₇ C ₃	/	/	/	/	/	/	?	/	5.3	8.33
M ₂₃ C ₆	/	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 ₇ C ₃	/	/	/	/	/	/	?	/	/	/
M ₂₃ C ₆	/	1.01	/	0.10	/	/	?	4.70	5.3	13.6

$$f_{vol}(\varphi_j) = \frac{f_m(\varphi_j)}{\sum_i \frac{\rho_{\varphi_i}}{\rho_{TaC}}} \quad \text{with } \rho_{TaC} = 14.5,$$

$$\rho_{M7C3} = 6.94 \text{ and } \rho_{M23C6} = 6.95 \text{ g/cm}^3$$

Calculations also showed the M₂₃C₆ → M₇C₃ change in Alloy 5, and revealed the presence of rare chromium carbides which were not observed in the alloys.

The calculated volume fractions' values do not correspond to the surface fractions ones, but it can be explained by a relation that seems exist between the two geometrical fractions:

$$\%vol = 1,65 \%surf \text{ for the TaC carbides}$$

$\frac{f_{surf} \varphi_i}{f_{vol} \varphi_i}$		Alloy 1	Alloy 2	Alloy 3	Alloy 4	Alloy 5
1200°C	MC	1.48	1.72	1.61	1.95	1.48
	M ₇ C ₃					0.73
1100°C	MC	1.23	2.12	2.08	1.56	1.53
	M ₇ C ₃					0.64
1000°C	MC	1.51	1.38	1.81	1.58	1.63
	M ₂₃ C ₆					0.39

CONCLUSIONS

Good fits were found for five different cobalt-based alloys, especially for the solidus temperatures. Concerning the nature of the phases, the expected carbide types were observed. Moreover, thermodynamical modelisation revealed for some compositions the presence of small quantities of others carbides not evidenced in the synthesised alloys. The rarefaction of carbides with an increasing exposition temperature is also confirmed by the simulation. Nevertheless values of carbides fractions are not similar, but it can be explained, at least for TaC carbides, by geometrical considerations.