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High temperature microstructures of ternary Co-30wt.% Cr - based alloys over the [0 to 2.0wt.%] carbon range

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Abstract

The Co-30wt.%-xC system was experimentally explored from x=0 to 2wt.%, by considering the stable microstructures at 1,000, 1,100 and 1,200°C, and the intervals of fusion. The strengthening potential and the refractoriness of several alloys belonging to this family were specified. Such simple alloys are able to display simultaneously a high amount of chromium for limiting hot corrosion, solidus temperatures as high as 1,300 °C and refractory carbides fractions that can reach 20 % in volume. Natures and fractions of carbides, and solidus temperatures were in good agreements with thermodynamic calculations. Inversely the measured liquidus temperatures were significantly higher than the calculated ones. In addition, thermodynamic modeling allowed to better interpret the disappearance of carbides due to oxidation at high temperature.

Keywords: High temperature alloys (A); Microstructure (C); Thermal analysis (D); Scanning electron microscopy (D); Thermodynamic modeling (D)

1. Introduction

Compared to nickel-base superalloys, cobalt alloys are generally not suitable for very high temperature application since they often need to be necessarily reinforced by carbides, the presence of which involves a decrease of refractoriness [1]. Indeed, they cannot be precipitation-hardened by intermetallic precipitates analogous to the γ' (Ni₃Al) of the nickel-base alloys, since such intermetallic compounds tend to be unstable at elevated temperature when present in a cobalt alloy [2]. Thus, their mechanical reinforcement is usually achieved by solid solution strengthening, or by carbides. These ones can be primary interdendritic carbides (appeared during solidification) [3], and/or fine secondary intragranular carbides (precipitated in matrix during a specific heat treatment) [4]. Generally, the presence of carbides induces a decrease of the refractoriness of these alloys, which bans their use for the hottest parts of turbines. However they remain interesting for high temperature applications when hot corrosion cannot be limited by alumina-growth on the surface of γ' -reinforced alloys, especially when the alloy is in contact for long times with molten substances (e.g. some glasses) that dissolve the Al₂O₃ outer scale [5-7]. In this field, the absence of the highly-oxidizable element Al and the possibility to obtain carbides at solidification with an element which necessarily belongs to the chemical composition to resist high

temperature oxidation and corrosion, let the simple ternary Co- Cr-C alloys family to be very interesting for both high temperature properties and easiness of fabrication. Indeed, this ternary system is already the base of more complex alloys which also include, for example, less than 10wt.% of Ni for stabilizing the FCC matrix at intermediate temperatures by preventing the appearance of the HCP low-temperature structure of cobalt [8], and some percents of Ta for obtaining highly refractory carbides [8-10], from which the compositions of numerous commercial cobalt-base superalloys. Otherwise, these ternary Co-Cr-C alloys can also be interesting without any addition. Firstly, they can be classically elaborated by foundry, under an atmosphere that can be more oxidizing than pure argon or vacuum. Secondly, they can potentially resist heat under low mechanical stresses (for very low carbides fractions) or on the contrary intensive stresses at lower temperatures (for high carbides fractions).

The aim of this study is to explore the high temperature microstructure characteristics of several different cobalt alloys belonging to the Co-30wt.% Cr-xC type, all with a chromium content particularly high for maximizing their hot corrosion resistance, and a carbon content which increases from very low values, allowing a high refractoriness, up to particularly high values potentially leading to a high mechanical strengthening effect.

2. Experimental details of the study

2.1. Selection of the alloys in the Co-Cr-C system

With nickel and iron, cobalt is one of the main pure elements that are not too expensive but the point of fusion of which is high enough. At room temperature cobalt is harder than the two other metals. Moreover, the melting temperature of pure cobalt is almost 50°C higher than nickel and its crystallographic network is face centered cubic at high temperature (even when it contains a great quantity of chromium), unlike iron which is back centered cubic (which is a cause of its mechanical weakness). Therefore, with a 30wt.% Cr, i.e. a high chromium content which is necessary to allow the formation of a Cr₂O₃-external scale and its maintenance for times long enough (since Cr diffusion is rather difficult in cobalt), the binary Co-30wt.% Cr is a good base for carbides-containing alloys. But, carbon must not significantly decrease the initial refractoriness of the binary alloy. In order to specify carbon contents that allow to maintain a high solidus temperature, Thermo-Calc [11] working with a database containing the descriptions of the Co-Cr-C system and of its sub-systems [12 - 17] was used.

On the {Cr=30wt.%}- section of the ternary phase diagram, displayed in Fig. 1, one can see that the solidus temperature remains almost constant until carbon reaches 1wt.% Beyond this content, its decrease versus the carbon content seems to accelerate. Then, the maximum value which was chosen for the carbon content is limited to 2wt.%, and the ternary alloys were selected over the 0 to 2.0wt.% C range (Table 1). Since the accuracy of thermodynamic calculations was not really known for the specific case of 30wt.% Cr, these alloys were elaborated in order to experimentally measure their intervals of fusion/solidification and to verify both the nature and fractions of carbides at the stable state for several high temperatures. This also allows to better know both the morphologies and the distributions of the carbides in the microstructure. Indeed, these characteristics of the carbides, which cannot be specified by thermodynamic calculations, can be also very important for high temperature properties.

2.2. Elaboration, metallographic preparation and observations

The seven alloys Co-30wt.% Cr-xC (x=0, 0.2, 0.4, 0.8, 1.2, 1.6 and 2.0wt.%) were synthesized from pure elements (99.9%, Alfa Aesar) by foundry, under 300mbars of argon U to avoid a possible loss of carbon, and thus to achieve the most precise possible carbon contents for the study. The furnace which was used is a CELES high frequency induction (300kHz) one. Fusion and solidification occurred in a copper crucible cooled by water circulation. The obtained ingots (all of about 100g) were cut in order to get, on the one hand small parts to measure the intervals of fusion and solidification, and on the other hand more important parts for the study of high temperature stable microstructures.

2.3. Measurements of the temperature limits of the mushy states

Differential Thermal Analysis (DTA) experiments were performed using a Setaram TGA 92-16.18 apparatus, in order to measure both the solidus and liquidus temperatures of the alloys. The thermal cycle used was composed by a heating rate of 20 °C/min up to 1200 °C, followed by a slower heating at 5 °C/min up to 1500 °C for a better accuracy in the temperature range of interest. Cooling was done first at 5 °C/min down to 1200°C, and second at 20 °C/min down to room temperature. Beginnings and ends of fusion and solidification were measured. The solidus and liquidus temperatures were supposed to be close to both the values obtained on the heating curve and the average value of the temperatures of the beginning (respectively end) of fusion and of the end (resp. beginning) of solidification.

2.4. High temperature exposures and metallographic characterization

Three samples of each alloy were prepared by cutting $10 \times 10 \times 3 \text{ mm}^3$ parallelepipeds from the ingot elaborated with the induction furnace, and all around polished with 1200-grit paper. They were exposed for 50 hours in the tubular resistive furnace of a Setaram TGA 92 thermobalance at 1,000, 1,100 and 1,200 °C under air at atmospheric pressure. These temperatures were reached with a heating at 20 °C/min. At the end of the 50 hours stage at high temperature, samples were cooled down to room temperature at 10 °C/min. The microstructures of the alloys were observed on embedded samples, prepared by cutting in two equal parts with a Buehler Isomet 5000 precision saw, and by embedding the two parts together in a mold using a cold resin system (Escil CY230 + HY956). Polishing was performed using SiC paper from 120 to 1200 grit under water, and finally with a 1µm diamond paste.

Metallographic observations were done using a Scanning Electron Microscope (XL30 Philips), essentially in the Back Scattered Electrons mode under an acceleration voltage of 20kV. The region of interest was always the middle of the sample's bulk, i.e. far from the zone affected by oxidation in most cases. The chemical composition of each alloy was verified at the same location, using the Energy Dispersion Spectrometry device of the SEM (only for Co and Cr, whose weight contents in the alloys and the molar masses of which are high enough). Two CAMECA microprobes were used for pinpoint analysis of the chemical compositions of the carbides (SX100 model, only in the samples the carbides of which were coarse enough, i.e. in the alloys with 0.8wt.%C or more) and of the matrix (SX50 model). If the carbides stoichiometries in the C-richest alloys were clearly determined by microanalysis, the natures of the carbides in the alloys with the lowest carbon contents (i.e. less than 0.4wt.%C) were deduced by comparison of gray levels with the carbides identified in the C-richest alloys.

The surface fractions of carbides were measured on three BSE micrographs taken on each sample with the SEM in BSE mode, in three different locations randomly chosen (magnification $\times 250$, areas of almost 0.1mm^2). The BSE detector leads to different levels of gray, depending on the average atomic number of the considered phase: the pixels of matrix (gray) and of chromium carbides (darker than matrix) were then well separated. The Photoshop CS software of Adobe was used on the three micrographs files of a same sample for measuring the carbides surface fractions. Each final surface fraction, average of three measures, was supposed to be close to the volume fractions.

The carbides volume fractions $f_v[\text{Cr}_x\text{C}_y]$, with $(x;y)=(7;3)$ or $(23;6)$, were also calculated from the mass fractions $f_w[\text{Cr}_x\text{C}_y]$ using equation (1):

$$f_v[\text{Cr}_x\text{C}_y] = \left(\frac{f_w[\text{Cr}_x\text{C}_y]}{\rho_{\text{Cr}_x\text{C}_y}} \right) / \left(\frac{f_w[\text{Cr}_x\text{C}_y]}{\rho_{\text{Cr}_x\text{C}_y}} + \frac{f_w[\text{matrix}]}{\rho_{\text{matrix}}} \right) \quad (1)$$

in which the mass fraction of carbides is deduced from the chromium weight content difference between the matrix and the whole alloy, according to equation (2):

$$f_w[\text{Cr}_x\text{C}_y] = \frac{W_{\text{Cr}}[\text{alloy}] - W_{\text{Cr}}[\text{matrix}]}{W_{\text{Cr}}[\text{Cr}_x\text{C}_y] - W_{\text{Cr}}[\text{matrix}]} \quad (2)$$

where $W_{\text{Cr}}[\text{alloy}]$ is the Cr weight content of the alloy, $W_{\text{Cr}}[\text{matrix}]$ the Cr weight content of the matrix analyzed by microprobe, and $W_{\text{Cr}}[\text{Cr}_x\text{C}_y]$ the theoretical Cr weight content of the Cr_xC_y carbides ($W_{\text{Cr}}[\text{Cr}_7\text{C}_3]=0.910$ and $W_{\text{Cr}}[\text{Cr}_{23}\text{C}_6]=0.943$).

The values used for the densities in g.cm^{-3} are 7.95 for matrix (from the weights and volumes of the samples), 6.941 for the Cr_7C_3 carbides and 6.953 for the Cr_{23}C_6 carbides [18].

2.5. Thermodynamic calculations

The measures performed on the alloys were compared to calculations performed using Thermo-Calc software version N and the database already mentioned above. These calculations lead to the solidus and liquidus temperatures, the chromium content of matrix, and the natures and mass fractions of the phases present at 1,000 °C, 1,100 °C and 1,200 °C.

3. Results

3.1. Microstructure observations

The Co00 logically presents an unique phase, and it is also almost true for the Co02 alloy since a second phase seems to exist but is very rare. Interdendritic carbides are more visible in the microstructure of Co04 but, in the sample exposed to 1,200°C, there are some bulk areas in which they are obviously absent; these areas correspond to surface parts where a serious surface oxidation can be noted. Carbides are sensibly denser in the case of Co08 at 1,000 and 1,100°C, while they are totally absent in the Co08 sample exposed at 1,200°C. The thickness of this sample is also significantly decreased after exposure compared to before: it seems to be due to a strong oxidation of the sample during its stage at 1,200°C, i.e. to the same phenomenon that affected some parts of surface of the Co04 alloy at this temperature.

For the three highest carbon contents (Fig. 2), the microstructure of the bulk was not affected by surface oxidation during the high temperature stages. Like for Co04 and Co08 in which the carbides were in sufficiently high fractions to begin to see the dendrites of matrix, the dendritic network is obvious for Co12, Co16 and Co20. Dendrites are separated from one another by areas involving both a part of matrix and carbides, with an eutectic morphology. The surface fraction of this eutectic increases with the carbon content but decreases when temperature increases, notably between 1,100 and 1,200°C. This is obviously accompanied by a noticeable change of morphology for the primary carbides. Secondary carbides, finer and dispersed in the dendritic volumes can also be seen in the C-richest alloys. For 1,000°C, their density seems to increase with the carbon content in the alloy (from Co12 to Co20) but these carbides disappear when the temperature increases, in all cases.

3.2. Solidus and liquidus temperatures

The Differential Thermal Analysis show a fusion and a solidification, in two times, with two peaks, logically more or less spread over an interval of temperatures when it is the eutectic compound or the matrix that is melting or solidifying (example in Fig. 3).

The temperature of solid-liquid transformation are plotted in Fig. 4. The solidus temperature is clearly dependent on the carbon content and there is a good correspondence between the experimental values and the ones calculated by Thermo-Calc. The highest solidus temperature is obtained with the binary Co00 alloy, while it drastically falls when a first little quantity of carbon (0.2wt.%) is added. Globally, from the Co02 to the Co20 alloy, there is a very slow decrease of the solidus temperature. On the contrary the experimental liquidus temperature is rather different from the calculated ones. It is notably true when the carbon content is far from the extremities of the [0; 2wt.%C] range, i.e. for Co04, Co8 and Co12 for which the experimental values are about 40°C higher than the calculated ones.

3.3. Nature and fractions of carbides

The carbides can be obviously seen only when the carbon content in the alloy is high enough (0.4wt.% and more). In most cases they are both really more black than matrix – what let think that their carbon content is among the highest possible – and with an acicular-type morphology in the eutectic compound, what let think more precisely that these carbides are Cr_7C_3 . They are also some cases where carbides are present enough to notice that their gray level is closer to the matrix one (e.g. Co04 at 1,000°C), as often seen in general about the Cr_{23}C_6 carbides. When the carbides size was high enough to allow performing accurate WDS microanalysis measurements, it appeared that carbides supposed to be Cr_7C_3 have effectively this stoichiometry. On the contrary, it was never possible to verify the Cr_{23}C_6 stoichiometry with the same apparatus, because of the too small size of the carbides in the Co04 and Co02 alloys. However their darkness which was close to the matrix's one allows to confirm that they are effectively of this stoichiometry. These observations are then in good agreement with the natures of carbides given by thermodynamic calculations (Table 2).

WDS microanalysis, performed in three different points in matrix, led to the chromium contents (average values +/- standard deviations) that are plotted in Fig. 5 (graphs in the first column) together with calculated values issued from Thermo-Calc calculations. Generally the measured chromium contents in matrix are consistent with calculations and the two sets of values show a same evolution versus the alloy carbon

content and versus temperature: the carbon content in matrix decreases almost linearly when the alloy carbon content increases, while, for all alloys, it conversely increases with temperature. The increase of the chromium content in matrix is logically related to the progressive disappearance of the carbides when the temperature increases, which was qualitatively noticed.

To more quantitatively describe the evolution of the presence of carbides, image analysis was performed on three randomly taken micrographs in order to obtain an average surface fraction and its corresponding standard deviation value, then an average mass fraction, for each alloy and each temperature when possible. No distinction were done between the Cr_7C_3 and Cr_{23}C_6 carbides when surface analysis was done, except for the rating of the gray level. The chromium content differences between matrix and alloy were also treated to deduce another experimental set of mass fractions of carbides (the values taken in equations (1) and (2) for the properties concerning the carbides were chosen thanks to the identification of carbides allowed by Thermo-Calc). All the obtained values of carbide mass fraction are represented, with the corresponding computed values added for comparison, in the graphs displayed in the second column of Fig. 5. The decrease of the carbide fraction when the alloy carbon content decreases is clearly seen in these graphs, on which Thermo-Calc also allowed to take into account the $\text{Cr}_7\text{C}_3 \rightarrow \text{Cr}_{23}\text{C}_6$ carbides change together with their mass fractions.

It appears first that image analysis led to carbides fractions that are closer to the calculated values than the mass fractions deduced from the measured chromium contents in matrix. Indeed the points for image analysis are very close to the calculated points, as long as carbides are still Cr_7C_3 . When Thermo-Calc shows that they are Cr_{23}C_6 a significant mismatch appears. Second, calculations show that the Cr_{23}C_6 carbides are effectively present only for the alloys with low carbon contents, and the carbon content under which they exist, decreases when temperature increases.

4. Discussion

4.1. Comments about the high temperature capability of these alloys

The presence of carbon in a Co-30wt.% Cr base alloy logically leads to carbides formed from the most carbide-former element which is moreover present in great quantity in the alloy, i.e. exclusively chromium carbides. These ones are logically more present when carbon is more present, a dependence which is almost linear considering the volume fraction but which can be sometimes less regular when a change from the Cr_7C_3 stoichiometry to the Cr_{23}C_6 one (with less carbon for a given quantity of metallic element) occurs. But even when the carbon content reaches 2.0wt.% the alloys remain hypoeutectic and the microstructure is still composed by a dendritic matrix and an interdendritic matrix-carbide eutectic, what is in good agreement with the 30wt.% Cr section of the Co-Cr-C phase diagram displayed in Fig. 1. Otherwise it is different from ternary Ni-30wt.% Cr-xC for which dendrites disappear when carbon is higher than about 1.5wt.% C (eutectic carbon content for this other family). Then, for ternary cobalt alloys, it appeared possible for the carbide volume fractions to go over 20% with conservation of a dendritic - then still continuous - matrix; therefore one can think that this system allows reaching a microstructure highly reinforced by interdendritic carbides and stable at high temperatures, as well as, after a heat treatment, by secondary carbides obtained in matrix which can help it to resist creep (noticeably at 1,000 and 1,100°C). The solidus temperature remains almost constant from the Co02 alloy up to the Co12 one, and thereafter it loses only few Celsius degrees with Co16, which allows the

maintenance of a high refractoriness that is also favorable for a good mechanical resistance at high temperature. Thus, following the needs of high temperature properties, on the one hand the Co-30wt.% Cr – C system can offer a high refractoriness with the Co00 alloy, the fusion of which begins at more than 1,400°C, which can be sufficient if no significant mechanical stresses are applied. On the other hand, this system can also provide a high density of interdendritic chromium carbides (Co-30wt.% Cr with more than 1wt.% C) with a refractoriness which remains at a high level (solidus temperature near 1,300°C). Indeed, the presence of a lot of carbides in interdendritic spaces can potentially enhance the tensile properties and creep resistance at high temperature (but also with a decrease of ductility) [1-2, 8], as it was previously observed for tantalum carbides in other 30wt.% Cr-containing cobalt-base alloys [19-21]. To finish, in almost all cases a good resistance against high temperature oxidation (but however lower than the similar nickel-base alloys which are usually more efficient in this field [5, 22-23]) is also achieved.

4.2. Comments about the correspondence between experimental measures and calculations

The DTA measurements allowed measuring temperatures of solid ↔ liquid transformations that can be compared to thermodynamic calculations. The two ways led to results that were consistent for the solidus temperatures, but the agreement is not so good for the liquidus temperatures, except when the difference between solidus and liquidus is particularly small, i.e. for low carbon alloys and for alloys near the eutectic composition. The real values of the matrix chemical composition are correctly found by calculations. It is also true for the natures of carbides which were clearly identified by WDS microanalyses when carbides were not too small (i.e. for Co08, Co12, Co16 and Co20), and which were found again by calculations. In the case of Co02 and Co04 for which it was not really possible to quantitatively identify the too small carbides by WDS microanalysis, the Thermo-Calc predictions about the natures of carbides were only verified by metallographic examinations. Indeed, when observed using the SEM in Back Scattered Electrons mode, $M_{23}C_6$ carbides are less dark than the M_7C_3 , while a Groesbeck etching (4 grams of $KMnO_4$ and 4 grams of $NaOH$ in 100mL of distilled water, immersion for 1 minute at room temperature) promotes a coloration of the $M_{23}C_6$ in brown and of the Cr_7C_3 in grey/blue. These colors allowed verifying, by optical microscopy observations, the natures of carbides in all the alloys, especially for the Co04 and Co02 alloys, and a good agreement with calculations was also found. Generally, thermodynamic calculations also led to carbides fractions that are close to the ones measured by image analysis. Thus, if the characteristics of solid alloys and the solidus-line equilibria are predicted with accuracy with the thermodynamic calculation tool which was used here, the description of the liquid phase must be improved to better represent reality. An accurate determination of the liquidus temperature can be very useful to specify technical parameters of foundry process (maximal temperature of melting, overheating to select) as well as to predict shrinkage defects and to modify geometries of cast pieces to prevent these problems. For that the databases of foundry simulation softwares need to contain good liquidus temperatures which are always easier and quicker to determine by thermodynamic calculations than by performing real DTA experiments.

4.3. Consequences of high temperature oxidation according to thermodynamic modeling

During their stage at 1,200°C, the Co04 alloy locally underwent a catastrophic oxidation to which a significant modification for the local bulk microstructure can be related. Indeed it was seen that in such areas carbides totally disappeared, while they always exist in neighbor areas where surface oxidation was not catastrophic. On the contrary the Co08 alloy lost its carbides over its whole thickness, after 50 hours at 1,200°C, because of the catastrophic oxidation that took place all around the sample. This local disappearance of carbides is not due to a decrease of the local chromium content since, on the contrary, chromium that belonged to carbides, was released in matrix. The Cr content of the latter increased up to about 30wt.% (i.e. to the value of the Cr content in the whole alloy) in the Co04 (locally) as well as in the Co08 as shown in Fig. 6 by the chromium profile performed across its whole thickness. The disappearance of carbides is due to the disappearance of carbon, as shown by Fig. 1 which indicates that the absence of carbide implied that the carbon content is probably zero and necessarily as least lower than about 0.1wt.%, i.e. about five (Co04) or ten times (Co08) the initial content.

Such phenomena did not affect neither the alloys with less carbon content, nor the alloys with higher carbon content. It is possible that the 0.4-0.8wt.% carbon range leads to matrixes which begin to be too impoverished in chromium by the presence of the chromium carbides, while these carbides are not yet dense enough to really accelerate the supplying of the oxidation front by grain boundary diffusion of chromium.

5. Conclusion

Simple ternary cobalt-base alloys are able to simultaneously contain a high amount of chromium to resist hot corrosion and a dense interdendritic network of carbides stable at high temperature useful for achieving high mechanical properties, without too marked decreasing of the solidus temperature which can stay at a very high level (i.e. close to 1,300°C). It is true that it is not possible to obtain simultaneously the very high level of refractoriness of the binary Co30Cr (above 1,400°C, useful for heat resistance when no intensive stresses are applied) and the high density of interdendritic carbides of the carbon-richest alloys of this study (favorable to a good mechanical resistance at high temperature). Nevertheless a good combination of these two properties can be obtained with the Co12 alloy for which the high reinforcement by carbides does not induce a significant decrease of the solidus temperature, by comparison to the very low carbon alloy Co02.

For chromium content equal to 30wt.%, the used database allows predicting microstructures with a sufficient accuracy in the solid state and when liquid is not the main phase present. Indeed experiments and calculations were often in good agreement in this condition but experiments gave additional information about the morphology and repartition of carbides (notably about a part of precipitated chromium carbides in matrix favorable to a good resistance against intragranular creep). On the contrary, since carbon cannot be measured by microanalysis because of its too low atomic mass and its too low weight content, thermodynamic calculations helps the experimental measures by allowing hypotheses about the carbon content in parts of the alloy where carbides disappeared, for example because of phenomena resulting from oxidation.

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TABLES

Table 1
Designation and carbon contents
of the studied alloys (base: Co-30wt.% Cr)

Alloy	Co00	Co02	Co04
C (wt.%)	0	0.2	0.4
Co08	Co12	Co16	Co20
0.8	1.2	1.6	2.0

Table 2
Types and mass fractions of matrix and carbides for 1,000, 1,100 and 1,200°C
as calculated by Thermo-Calc (the matrix is FCC in all cases, for Co00 too)

Alloys	1,000°C		1,100°C	1,200°C
Co20	M7C3 (21.73wt.%)		M7C3 (21.11wt.%)	M7C3 (20.21wt.%)
Co16	M7C3 (17.32wt.%)		M7C3 (16.81wt.%)	M7C3 (16.05wt.%)
Co12	M7C3 (12.90wt.%)		M7C3 (12.46wt.%)	M7C3 (11.82wt.%)
Co08	M23C6 13.33wt.%	M7C3 0.17wt.%	M7C3 (8.09wt.%)	M7C3 (7.52wt.%)
Co04	M23C6 (6.57wt.%)		M23C6 (5.95wt.%)	M7C3 (3.18wt.%)
Co02	M23C6 (3.04wt.%)		M23C6 (2.49wt.%)	M23C6 0.64wt.% M7C3 0.61wt.%

FIGURES

Fig. 1. Choice of the carbon content range considering the solidus temperature according to Thermo-Calc, and positions of the studied alloys in the {30 wt.% Cr} section of the Co-Cr-C phase diagram

Fig. 2. Microstructures at high temperature of the three carbon-richest alloys (pictures taken with MEB in BSE mode)

Fig. 3. Example of a Differential Thermal Analysis curve (here performed on the Co16 alloy): positions of the points leading to the characteristic temperatures

Fig. 4. Evolution of both the liquidus and solidus temperatures when the carbon content increases from 0 to 2wt.%, according to Thermo-Calc (Computed) and to experimental measures of beginning and end of fusion and solidification (1: heating part only, 2: average heating+cooling parts)

Fig. 5. Evolution of both the chromium content in the matrix and the carbides volume fractions when the carbon content increases from 0 to 2wt.%, according to calculations (Th.-Calc) and to experimental measures (WDS microprobe, deduction from the Cr content alloy/matrix differences, image analysis)

Fig. 6. Carbide losses in Co-30wt.% Cr-C bulks due to catastrophic oxidation:
 Top (Co04 1,200°C): a place having kept its carbides except in an outer zone
 Bottom (Co08 1,200°C): all the thickness has lost its carbides but the Cr content mainly
 staid at 30wt.%