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(Online First) Thermal Properties of a Cobalt-based Superalloy Designed to be Reinforced by Titanium Carbides and Chromium Carbides

Mira Khair, Patrice Berthod

Institut Jean Lamour, Université de Lorraine Faculty of Science and Technologies, Campus Victor Grignard, Boulevard des Aiguillettes, Postal Box 70239, 54506 Vandoeuvre-lès-Nancy Cedex, France

ABSTRACT

In this study titanium carbides were considered to strengthen alloys elaborated by classical foundry and displaying a polycrystalline structure. A model alloy, whose composition is Co(bal.)-25Cr-0.5C-1Ti (wt.%), serves as a kind of prototype to test the possibility of formation of TiC carbides during solidification and the thermal resistance of these particles at elevated temperature. This alloy was synthesized by high frequency induction melting under inert atmosphere and was subjected to microstructure characterization, Differential Thermal Analysis and exposure at 1100°C for about two days. A dendritic cobalt-based matrix was obtained with, in the interdendritic spaces, chromium carbides and titanium carbides. The melting point measured by DTA is slightly below 1300°C and the titanium carbides well resisted to the exposure at high temperature. On-going tests carried out to assess the mechanical behavior at high temperature suggest rather high potential of creep resistance at 1100°C.

Keywords: *cobalt-based alloy, titanium carbide, refractoriness, high temperature, microstructure stability*

1. Introduction

1.1 Properties required for superalloys in service at high temperature

Many applications at elevated temperature involve very severe conditions of working for the used materials. For example the hottest components may be exposed at temperatures exceeding 1,000°C and, at the same time, they must transmit significant mechanical forces and they are simultaneously in contact with particularly aggressive hot fluids (mixtures of oxidant gases, corrosive molten substances)^[1,2].

1.2 Cast cobalt-based superalloys instead /' single crystalline superalloys

Among the superalloys which are currently available for constituting components for high temperature service in hard mechanical and chemical working conditions the Nickel-based /' single crystals are still the ones which offer the best performances. Protected by thermal barrier coatings (TBC) from the extremely hot gases coming from the combustion chambers, they know limited high temperatures (less than 1,100°C). This allows their gamma prime precipitates remaining stable and efficiently reinforcing the alloys on long time. But when the hot components cannot be covered by zirconia deposits whatever the reason these /' single crystalline superalloys lose their superiority because of the disappearance of their intermetallic reinforcing particles during long stages at temperatures between 1,000 and 1,100°C^[3,4]. For such conditions some of the polycrystalline superalloys can be envisaged. Cobalt is the main element present in rather old superalloys elaborated by classical foundry^[1-4]. Chromium is almost systematically present in these alloys as second main element to give them great resistance against both oxidation by gases and corrosion by molten salts and CMAS (turbine blades and disks in the aeronautical engines) or glasses (glass-forming tools)

at high temperature^[5,6]. The mechanical strengthening can be achieved using solid solution hardening (tungsten, molybdenum, tantalum ... atoms distorting the crystalline network and obstructing the dislocations movement) or by carbides: primary carbides interlocking neighbor solidification dendrites, secondary carbides pegging dislocations)^[1-4].

1.3 MC carbides used as efficient strengthening particles in Co-based superalloys

The carbides present in the chromium-containing cobalt-based superalloys can be simply chromium carbides (Cr_{23}C_6 in low carbon containing alloys or, Cr_7C_3 in medium/high carbon containing alloys). In such case the reinforcement is at a correct level for not too high service temperatures ($1,000^\circ\text{C}$ and below) and a beneficial effect is also obtained in the field of hot oxidation and corrosion since these carbides constitute chromium reserves in the grain boundaries and interdendritic spaces from which the Cr atoms are able to rapidly diffuse toward the oxidation front to create and maintain the protective chromia scale [5,6]. However, at temperatures higher than $1,000^\circ\text{C}$, the chromium carbides rapidly evolve in terms of volume fraction (decrease) and morphology (coalescence), with as consequence the loss of their strengthening effect. Fortunately other efficient alloy-strengtheners carbides can be used for long time at temperatures close to $1,100^\circ\text{C}$ or higher: some MC-type carbides. The most used among them are tantalum monocarbide (TaC) but other were also recently considered, such as HfC or ZrC [7,8]. When crystallizing at the end of solidification by forming a eutectic compound with matrix, these carbides appeared as script-like particles mixed with the peripheral parts of the pro-eutectic dendrites. This allows these MC-carbides constituting a hard interdendritic network interlocking dendrites. This mechanically beneficial effect remains on long duration at high temperature since these MC carbides rather well resist to volume fraction and morphological evolution.

1.4 Ti used as MC-former element in polycrystalline cobalt-based superalloys

TaC, HfC, ZrC remain rather stable at high temperature with as consequence an interesting sustainability of their strengthening effect. Unfortunately the involved elements are expensive (notably Hf, but also Zr and Ta) and the volume mass or density of the obtained carbides is rather high (7 g/cm^3 for ZrC, 12 g/cm^3 for HfC, 14.5 g/cm^3 for TaC). With less than 5 g/cm^3 another MC-type carbide, furthermore formed from a cheaper element, can be also interesting: the titanium monocarbide: TiC. Indeed, Ti which is known as a base element for light alloys (e.g. TA6V [10] or as aluminide-former [11] or γ -former [12] element, may form TiC at solidification in some chromium-rich superalloys, not based on nickel [13-15] but on cobalt [16]. Obviously, by regards to what happens in the as-cast microstructures of nickel-chromium alloys containing titanium (chromium carbides precipitate preferentially to TiC carbides), TiC can be successfully obtained in the microstructures of cobalt-chromium alloys, with in addition a script-like morphology as the eutectic TaC, HfC and ZrC. This let hoping that TiC carbides can be used instead the expensive and heavy TaC carbides (for instance) with a similar strengthening effect. But the sustainability of these TiC carbides must be verified. This is the main objective of the present work.

2. Choice of the studied alloy, elaboration and as-cast microstructure

2.1 The alloy subject of the study

The chemical composition under consideration in this work is Co(bal.)-25Cr-0.5C-1Ti, all contents being given in weight percent. 25 wt.%Cr is chosen to favor a good behavior of the alloy in oxidation at high temperature; 0.5 wt.%C may allow obtaining a interdendritic carbide network dense enough to really strengthen the alloy but not interconnected to preserve high impact toughness and to avoid problems of too easy crack propagation. The titanium content was rated in order to promote the formation of both TiC carbides to achieve, combined with the hard cobalt-based matrix, good mechanical properties at high temperature, as well as chromium carbides for their strengthening effect at moderate temperature and for their role of chromium reservoirs located in the interdendritic spaces for improving the oxidation and corrosion resistance at high temperature. For that the weight content chosen for Ti was defined to correspond to half the atomic content of carbon. It is thus expected that a half part of the carbon atoms will be involved in the formation of titanium carbides and the second half in the formation of chromium carbides.

2.2 Preliminary thermodynamic calculations

Prior to the real elaboration thermodynamic calculations were carried out to verify whether the wished microstructure can be expected to be really obtained. These calculations were performed using the N version of the Thermo-Calc software and a modified version of the SSOL database. First, sections of the quaternary diagram were computed (Figures 1-2). One can see that, according to these two isopleth sections, solidification should start with the nucleation and the subsequent growth of crystals of matrix, over two or three tens of Kelvin, followed by the nucleation

and growth of titanium carbides. After almost one hundred Kelvin of additional cooling, the residual liquid should start a ternary eutectic transformation:



at constant temperature (about 1570K as is to say about 1300°C).

After solid state cooling of about 300K, the {high temperature}-type of chromium carbide (M_7C_3) would transform into the {low temperature}-type of chromium carbide (M_{23}C_6), and after a little more than 100K of additional solid state cooling, this is the {high temperature}-type of the matrix (Face centered Cubic/FCC) which should transform into the {low temperature}-type of matrix (hexagonal compact/HCP). Below 1000K (i.e. about 700°C), taking into account the rather fast cooling which is expected occur practically, it can be considered that the final microstructure may look like a triple-phased state: hexagonal compact Co-based matrix containing a part of Cr, Ti and C in solid solution, titanium carbides and chromium carbides. Furthermore it is possible that the matrix can be itself double-phased: hexagonal compact Co-solid solution + a residual part of FCC Co-based solid solution) while the chromium carbide phase can be constituted of M_{23}C_6 and of residual M_7C_3 . Indeed, the rather fast solid state cooling can be expected to do not allow the total transformation in both cases.

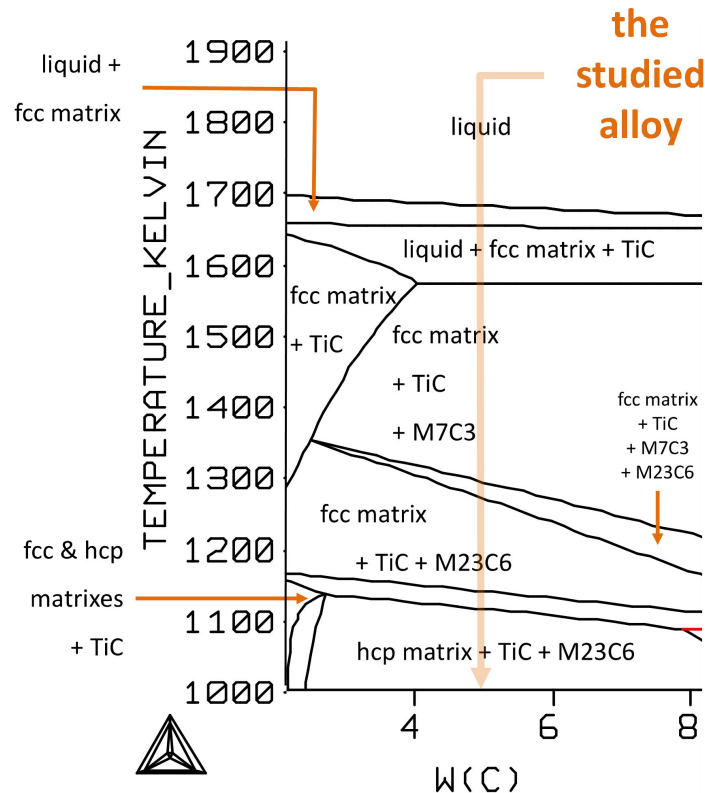


Fig. 1 Position of the studied alloy in the C-varying {Co(bal.)-25Cr-1Ti}-isopleth section of the Co-Cr-Ti-C quaternary diagram

A final observation that can be done by considering these two isopleth sections is that the vertical straight line crosses the successive double-phased and triple-phased domains by their middles. Consequently, even in case of small deviation in Ti content or in C content, the development of microstructure during solidification and solid state cooling, as well as the final microstructure, are expected to be qualitatively the same as described above.

The theoretical development of the microstructure of the alloy and the possible solid state transformation during post-solidification cooling can be anticipated quantitatively by performing calculations for temperatures lower and lower. The graphs plotted in **Figure 3**, which are in accordance with the previous isopleth sections in term of temperatures (liquidus and solidus, temperatures of carbide-type change and of matrix-type change), allow knowing better the mass fractions of phases: one can see that a little more than 1mass.% of TiC and about 4 mass.% of

chromium carbides may be expected.

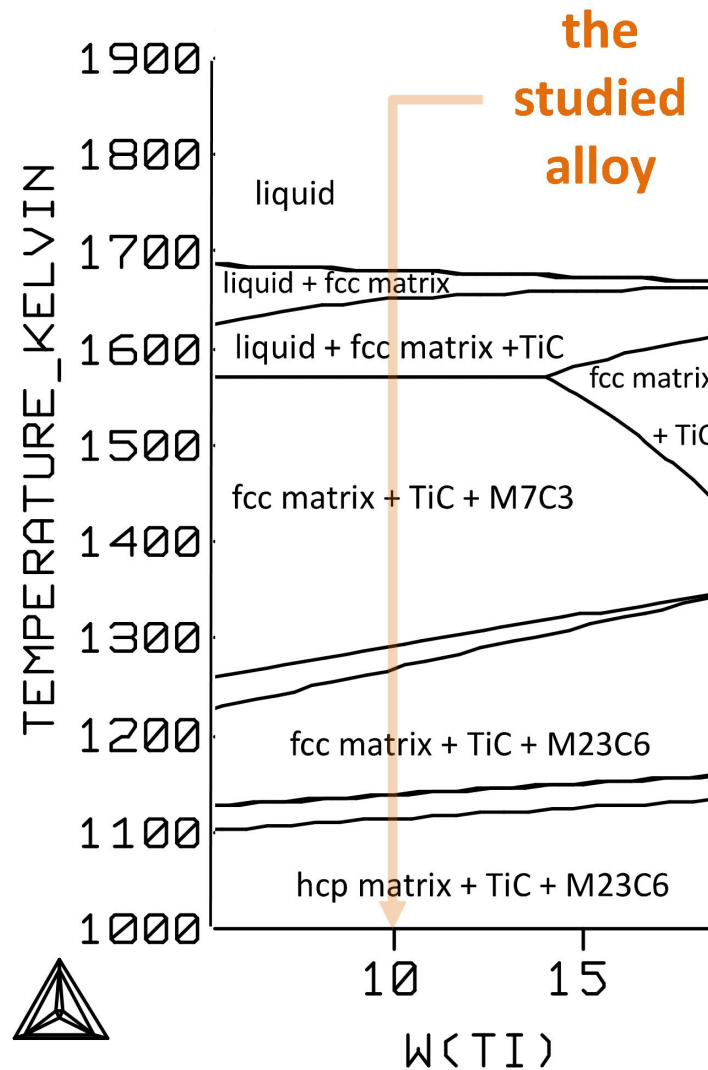
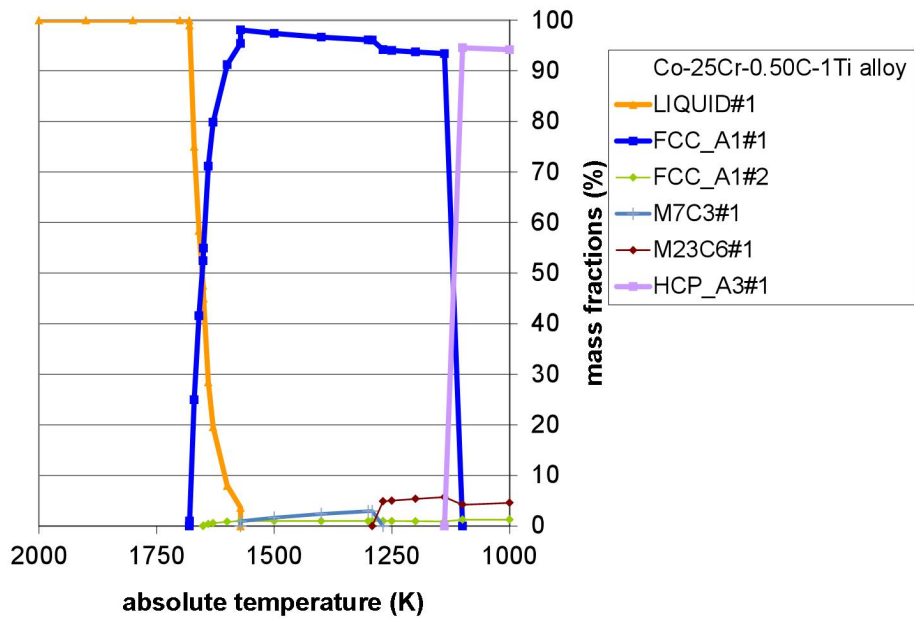


Fig. 2 Position of the studied alloy in the Ti-varying {Co(bal.)-25Cr-0.5C}-isopleth section of the Co-Cr-Ti-C quaternary diagram

2.3 Real elaboration of the alloy and obtained microstructure

The charge to melt was prepared from pure elements (Alfa Aesar, purity > 99.9% in weight). Parts of pure element were placed together in the segmented copper crucible of a 50kW High Frequency Induction Furnace (CELES, France). A silica tube was placed around the crucible and closed at both extremities, and the initial internal local atmosphere (laboratory air) was replaced by an inert atmosphere constituted of 300 millibars of pure argon by three-times pumping until primary vacuum and pure Ar introduction. Heating was



↑
Full range display

Enlargement of the low-contents part

↓

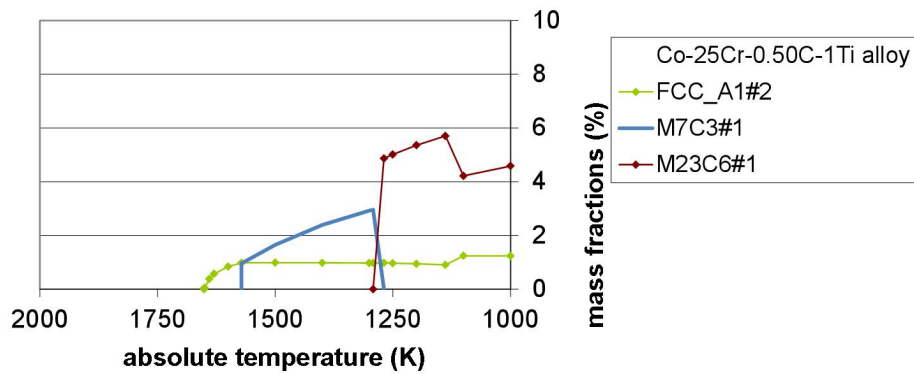


Fig. 3 The expected solidification sequences as predicted by Thermo-Calc

carried out by respecting two stages, a first one to allow homogenous heating in still solid state (30 seconds at 2500 Volts / 110kHz) and a second one to achieve total melting and liquid homogenization (5 minutes at 5000 Volts, 110kHz). The decrease in applied voltage was continuously realized during about one minutes and the levitating liquid alloy cooled and took in touch with the internally water cooled copper crucible. Solidification was rather fast as well as the solid state cooling (ingot at room temperature about 25 minutes after solidification). The on-going melting and the obtained ingot are shown in **Figure 4**.



On-
going
melting



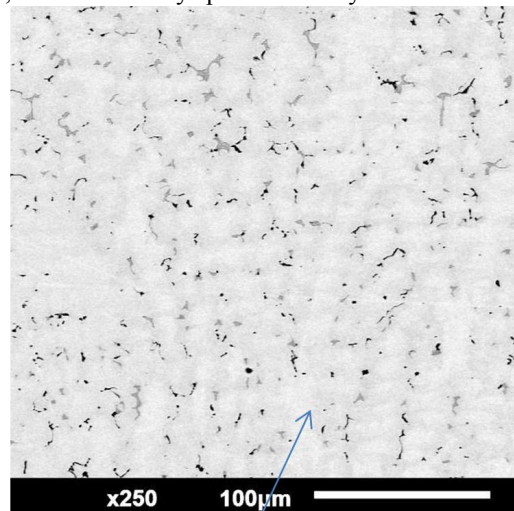
Obtained
ingot

Fig. 4 Photographs of the melting of the initial metallic charge and of the solidified ingot cooled down to room temperature and extracted from the crucible

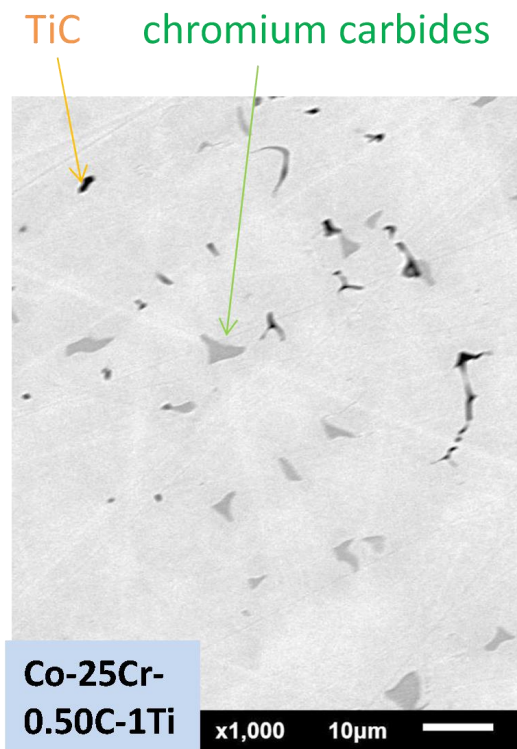
The ingot was cut to allow preparing a metallographic sample for characterizing the microstructure of the alloy in its as-cast state. This part was embedded in a metallographic cold resin mixture (ESCIL, France) and ground/polished until mirror-like state using #240 to #1200-gritSiC papers and textile disk containing 1 μ m-sized hard particles. The as-cast microstructure was observed using a Scanning Electron Microscope (SEM, JEOL JSM 6010LA) and analyzed using an Energy Dispersion Energy device (EDS) attached to the SEM. The imaging mode was the Back Scattered Electrons (BSE) one.

The as-cast microstructure is illustrated in **Figure 5**. The matrix structure is clearly dendritic, as clearly revealed the carbides located in the interdendritic spaces. Since all other phases (all of the carbide type) are interdendritic matrix was really the first solid to crystallize at beginning of solidification. This confirms what was suggested by calculations

(isopleth sections and graphs, Figures 1-3). The black interdendritic particles and the gray ones are titanium carbides and chromium carbides respectively, as confirmed by spot EDS analyses.



Co(Cr, Ti) matrix



Co-25Cr-
0.50C-1Ti

Fig. 5 SEM/BSE micrographs of the as-cast microstructure of the as-cast alloy (top: general view, bottom: magnified view)

2.4 Differential Thermal analysis

The calculated results brought by Thermo-Calc indicated above that the alloy was rather refractory with a solidus temperature of about 1575 K or 1300°C. However, before performing high temperature exposure it can be useful to verify that experimentally. A Differential Thermal Analyzer (DTA, SETARAM , France) was used to measure the solidus and liquidus temperature. The applied thermal cycle was +20K/min until 1200°C, +5K/min from 1200 to 1500°C, -5K/min from 1500°C to 1200°C and -20K/min for cooling until room temperature. **Figure 6** presents a photograph of the DTA apparatus (top) and the obtained thermal curve (bottom).

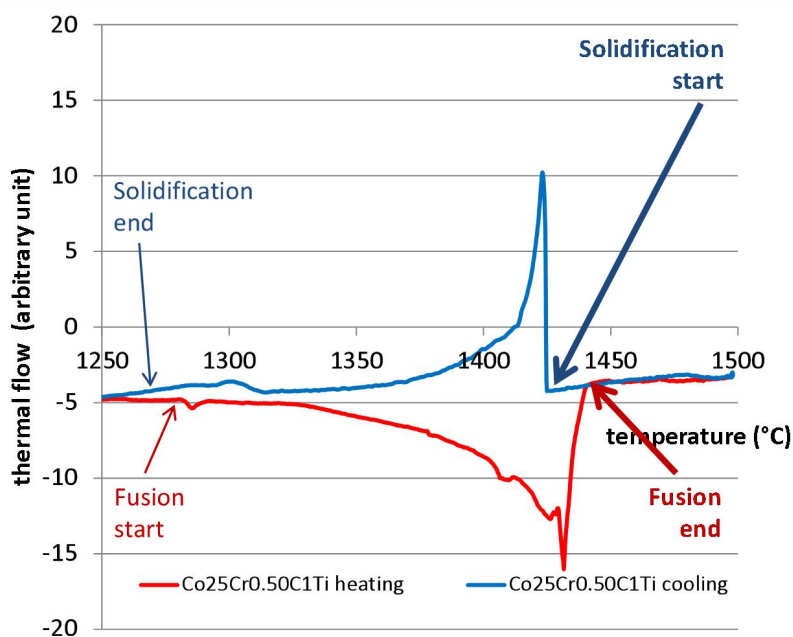


Fig. 6 The DTA apparatus and the obtained curve

The heating part (in red) is affected by a first small peak of heat absorption before reaching 1300°C while the major part of heat absorption occurs from about 1340°C up to near 1450°C. The cooling part of the curve (in blue) is characterized by a sudden release of heat. Obviously delayed nucleation led to overcooling with as consequence this abrupt jump in released heat. This goes on until about 1330°C, before a new bump spread from 1320°C down to just above 1250°C. First comments that can be done are the interpretation of the two main heat absorption and the two main heat releases. The low temperature ones (with the smallest areas under curves) may correspond to the melting of the eutectic part of the alloy mixing matrix and carbides. The high temperature ones can be certainly attributed to the melting and new crystallization of the dendritic matrix.

2.5 High temperature evolution of the microstructure

Taking into account that its melting start temperature is obviously lower than 1300°C, the alloy is probably too weak mechanically at 1200°C and maybe also 1150°C. The temperature of interest for the thermal test for the

microstructure was thus chosen as 1100°C. This temperature is the typical one of significant destabilization of the gamma prime precipitates reinforcing the Ni-based single-crystalline superalloys. A second part of alloy cut in the ingot was thus exposed at 1100°C for 46 hours in a resistive furnace. After this isothermal stage, the sample was extracted out the furnace and rapidly cooled by air quenching. The same metallographic preparation as described above for the as-cast part was done and the mirror-like cross-section was observed with the SEM. It appeared that, despite the rather long exposure and the particularly high temperature of test the microstructure did not evolved significantly, as illustrated in **Figure 7**. Indeed the chromium carbides were partly lost but the titanium carbides remained globally stable.

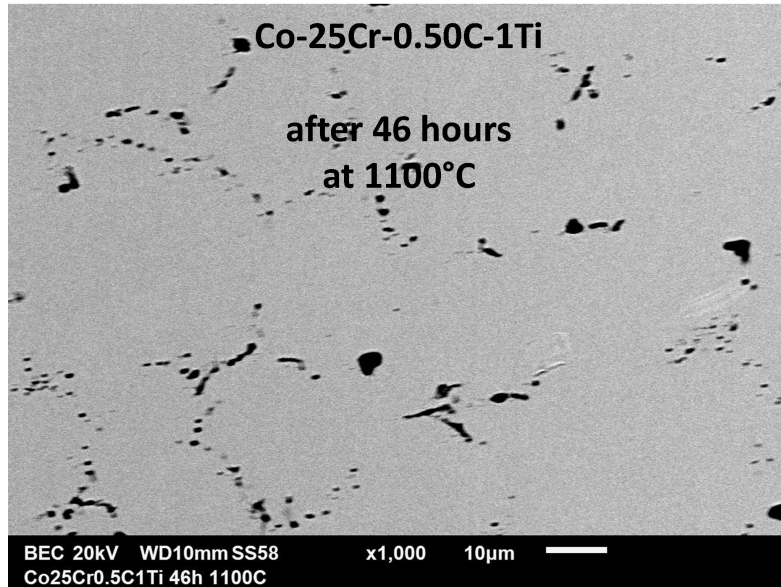


Fig. 7 The microstructure of the alloy after 46 hours spent at 1100°C (air quenching)

2.6 Comparison of the calculated theoretic results and the experimental results

In order to estimate the accuracy of the database used for the thermodynamic calculations the calculated temperatures of liquidus and solidus were compared to the melting start/solidification end and melting end/solidification start temperatures, the calculated chemical composition of matrix stabilized at 1100°C was compared to the average values determined from three spot EDS measurements and the volume fractions of titanium carbides and of chromium carbides deduced from their calculated mass fractions were compared to results of image analysis (average and standard deviation determined by image analysis using the Photoshop software) performed on SEM/BSE micrographs taken in three randomly chosen areas.

Concerning the temperature limits of the mushy zone range one can see that good agreement exists for the liquidus temperature between the calculated theoretic values and the experimental ones determined by DTA (Table 1) while some mismatch must be noticed for the solidus temperature. Concerning the stable state at 1100°C (Table 2) there is little discrepancies for the Cr and Ti contents (real Ti and Cr contents both a little higher than the theoretic ones) while the two TiC volume fractions are consistent. This is not the case for the volume fraction of the chromium carbides, which are significantly rarer in the real alloy than predicted. However this later observation is consistent with the higher Cr content in matrix in the real alloy by comparison with the calculated one: if there is less chromium carbides there are logically more chromium in solid solution in the matrix.

Thermo-Calc	Differential thermal analysis	Consistent ?
Liquidus temperature (°C)	Fusion end's temperature (°C)	Yes / No
	Average value (°C)	
	Solidification start's temperature (°C)	
	1440	

1407	1433	YES
	1299	
Solidus temperature (°C)	Fusion start's temperature (°C)	Yes / No
	Average value (°C)	
	Solidification end's temperature (°C)	
1299	1278	NO but not very far
	1275	
	1271	

Table 1 Comparison of the calculated liquidus and solidus temperatures and the measured ones for the Co-25-0.50C-1Ti alloy

Temperature	FCC Co-based matrix		TiC carbide		^a M ₇ C ₃ or ^b M ₂₃ C ₆ carb.	
	Th.-Calc	Exp.	Th.-Calc	Exp.	Th.-Calc	Exp.
1373.15K (1100°C)	Chem. compo: 75.968 Co 23.701 Cr 0.237 Ti 0.094 C	Wt.% in Cr and Ti: Bal. 25.5 ±0.3 0.4 ±0.1 Not meas.	0.979 mass.% i.e. 1.599 vol.%	average ± std dev (surf.%) 1.62 ± 0.22	^a 2.558 mass.% i.e. ^a 2.964 vol.%	average ± std dev (surf.%) 0.23 ± 0.40

Table 2 Comparison of the metallurgical states at 1100°C of the Co-25Cr-0.50C-1Ti alloy as calculated by Thermo-Calc (Th.-Calc) and as really obtained (Exp.)

3. Conclusions

A cobalt-based alloy rich in chromium for resisting high temperature oxidation and corrosion and strengthened by both chromium carbides and by titanium carbides was successfully obtained. This alloy is not so refractory as other alloys based on Co and containing the same Cr, C and MC-former metallic element (Ta, Hf^[7,8]) but the titanium carbides which formed at solidification are stable at elevated temperature on long time. Associated to a cobalt dendritic matrix intrinsically very resistant mechanically at high temperature, these interdendritic carbides may lead to a new superalloy concept, base of future developments. Before envisaging any optimization it is judicious to preliminarily verify the high temperature creep resistance and oxidation behavior of this model alloy. First results^[17] seem allowing to hope properties effectively of interest in these fields (at least about the mechanical behavior).

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