

As-Cast Microstructures and Hardness of Chromium-Rich Cobalt-Based Alloys Reinforced by Titanium Carbides

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Abstract

Three cobalt-based alloys containing chromium for good chemical resistance at high temperature and both carbon and titanium in quantities great enough for expecting developing significant TiC network to mechanically reinforce them at high temperature, were synthesized by foundry. This Co-25Cr-0.25C or 0.50C-1Ti or 2Ti (all contents in wt%) were successfully obtained, thanks to the fusion and solidification both in inert atmosphere. The obtained microstructures were composed of a dendritic matrix and of interdendritic carbides, mainly of the TiC composition in the three alloys but chromium carbides are also present, notably in the Co-25Cr-0.50C-1Ti. The titanium carbides are of the script-like morphology and are imbricated with matrix in the interdendritic spaces, seemingly forming a eutectic compound with it. The higher the carbon content, the more numerous the carbides whatever their nature, and the higher the titanium content the more numerous the titanium carbides. The hardness is of about 300Hv₁₀ Kg for the 0.25C-containing alloy and of about 370Hv₁₀ kg for the two 0.5C-containing ones. Some particles looking more or less as titanium carbides are rather titanium carbonitrides Ti(C,N) et the presence of titanium oxides was observed in some locations in the bulk. Obviously the elaboration protocol using commercial argon is not well adapted to the strong tendency of titanium to react with O and N.

Keywords: Cobalt alloy; Titanium carbides; Casting; Inert atmosphere; As-cast microstructure; Hardness; Titanium carbonitrides

Introduction

Beside the famous gamma/gamma prime single-crystalline nickel-based superalloys [1-3], some of the conventionally cast equiaxed superalloys merit to be considered too because it was recently demonstrated that some of them are able of high temperature mechanical [4,5] and chemical [6,7] performances of the same level that Ni-based single-crystals. Notably, the cobalt-based alloy containing eutectic script-like eutectic MC carbides, which are remarkably stable at high temperature almost whatever the M carbide-forming element - Ta, Nb, Hf, Zr... [8] - may offer, for elevated temperatures, high levels of mechanical performance, and eventually of chemical resistance. Such interesting high temperature properties were first noticed with TaC-containing cobalt-based superalloys [9], in the mechanical [10], {molten substances}-induced corrosion [11] or air-oxidation [12] fields. Promising high temperature properties are expected with cobalt-based alloys strengthened by

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Hafnium(IV) carbides (HfC) [13], in the mechanical field [14] as well as in the oxidation one [15]. Niobium carbides (NbC) were also considered and recently tested in Co alloys [16].

Titanium, which is commonly rather considered as a base-element for light aeronautic alloys [1-3] or orthodontic arch-wires [17] for examples, or which can be used in the nuclear field for its specific behaviour in contact with molten glasses [18,19], can also be considered for the reinforcement of superalloys by exploiting its strong carbide-former character. Lighter than Ta or Zr, more available on earth than Hf, better in high temperature oxidation than Nb, it merits to be tested in this role of MC-former element. This is what was done in this work, with the elaboration by casting of three cobalt-based alloys containing 0.25 wt% to 0.5 wt% C (in the superior average of the carbon range usually adopted for superalloys), 25 wt% Cr for the resistance against both oxidation and corrosion at high temperature, and 1 wt% or 2 wt% Ti in order to obtain either exclusively TiC carbides (0.25 wt% C+1 wt% Ti and 0.50 wt% C+2 wt% Ti) or a mixed population of carbides composed of TiC for a half and of chromium carbides for the second half part.

Experimental

These three alloys (Co-25Cr-0.25C or 0.50C-1Ti or 2Ti, in wt%) were synthesized from pure elements (Co, Cr and Ti from Alfa Aesar, >99.9 wt% purity, C: pure graphite rods from Sigma-Aldrich, >99.99 wt% purity) by melting under inert atmosphere (300 mbars of pure Ar, total impurities (O₂, H₂O, N₂): <5 ppm) using a high frequency induction furnace (CELES). The obtained ingots (about 40 g for each of them, conical geometry with a 20 mm height and a 20 mm base diameter) were cut using a metallographic saw (BUELHER).

A part per alloy was taken near the centre of the ingot to characterize the as-cast microstructure. They were embedded in a cold resin/hardener mixture (ESCIL), ground with successive SiC-containing papers of grade varying from 120 to 1200, ultrasonically cleaned, then polished with a textile disk enriched with 1 µm alumina particles. The obtained mirror-like metallographic samples were examined using a Scanning Electron Microscope (SEM) from JEOL (type JSM-6020LA) in Back Scattered Electrons (BSE) mode to control the microstructures of each of the three alloys. The Energy Dispersion Spectrometry (EDS) device equipping the SEM allowed controlling their chemical composition.

The hardness of the three alloys was specified by Vickers indentation under a load of 10 kg. Ten indentations were carried out per alloy, using a Testwell Wolpert machine. The average value and the standard deviation one were calculated.

Results and Discussion

The as-cast microstructure of the first alloy, the Co-25Cr-0.25C-1Ti one, is illustrated by two SEM/BSE micrographs in FIG. 1, one giving a general view (120X) and the second more detailing the microstructure (500X). One can well see on the general view that the microstructure is clearly dendritic and that there are dark particles which appear, in the detailed view, as having a tendency to be script-like shaped. One must notice that there are also rare coarser dark particles (general view). The EDS measurements carried out on three different locations leads to the average contents in Co, Cr and Ti presented in TABLE 1 (C cannot be measured by this technique: too light element and with content too low). Globally the targeted composition was effectively obtained.

The as-cast microstructures of the Co-25Cr-0.50C-1Ti alloy is displayed in FIG. 2, with two SEM/BSE micrographs again (general view at 120X, more detailed one at 500X). The dark particles are significantly more numerous (and the coarse dark

particles too). The ones that one can think as being carbides reveal here too the dendritic character of the matrix. At the highest magnification, except the coarse globular particles, the dark (black) particles seems being TiC, as suggested by their tendency to the script-like. Other particles are present, a little clearer: they are maybe the chromium carbides that were expected since there is twice more carbon atom than titanium atoms in this alloy. The chemical composition is here too consistent with the targeted one (TABLE 2).

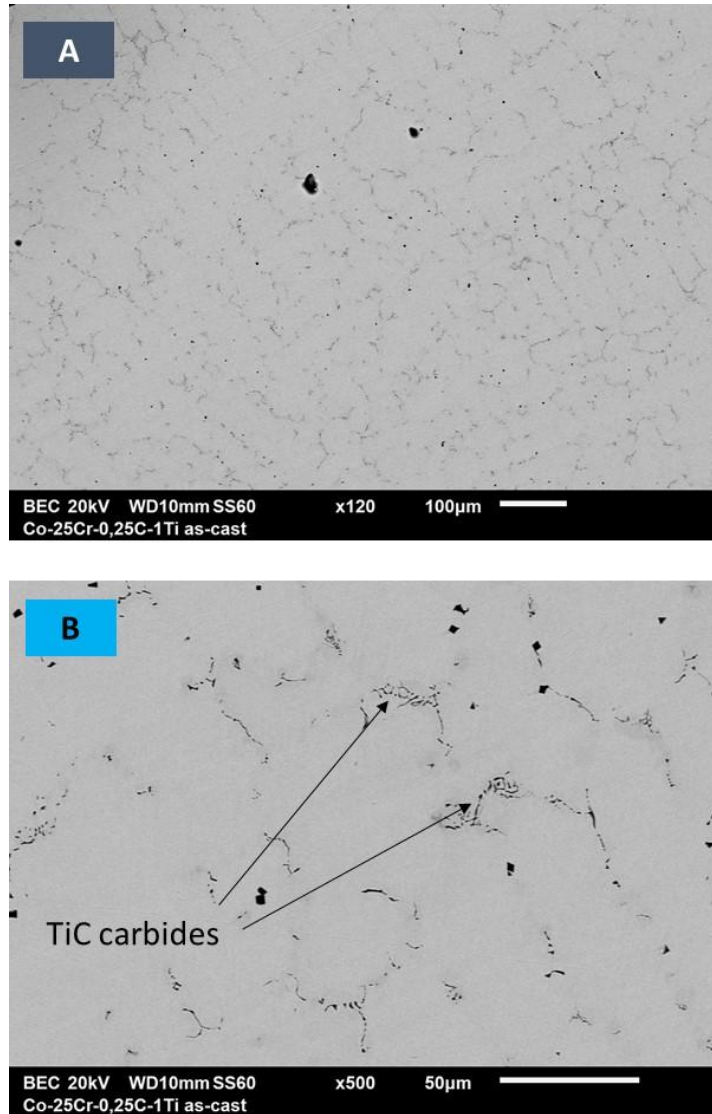


FIG. 1. General (A) and detailed (B) views of the as-cast Co-25Cr-0.25C-1Ti alloy (in wt%) when observed with the SEM in BSE mode.

TABLE 1. Chemical composition of the Co-25Cr-0.25C-1Ti alloy.

0.25C-1Ti	Co (wt%)	Cr (wt%)	Ti (wt%)
Average	73.60	25.59	0.83
SD	0.53	0.42	0.11

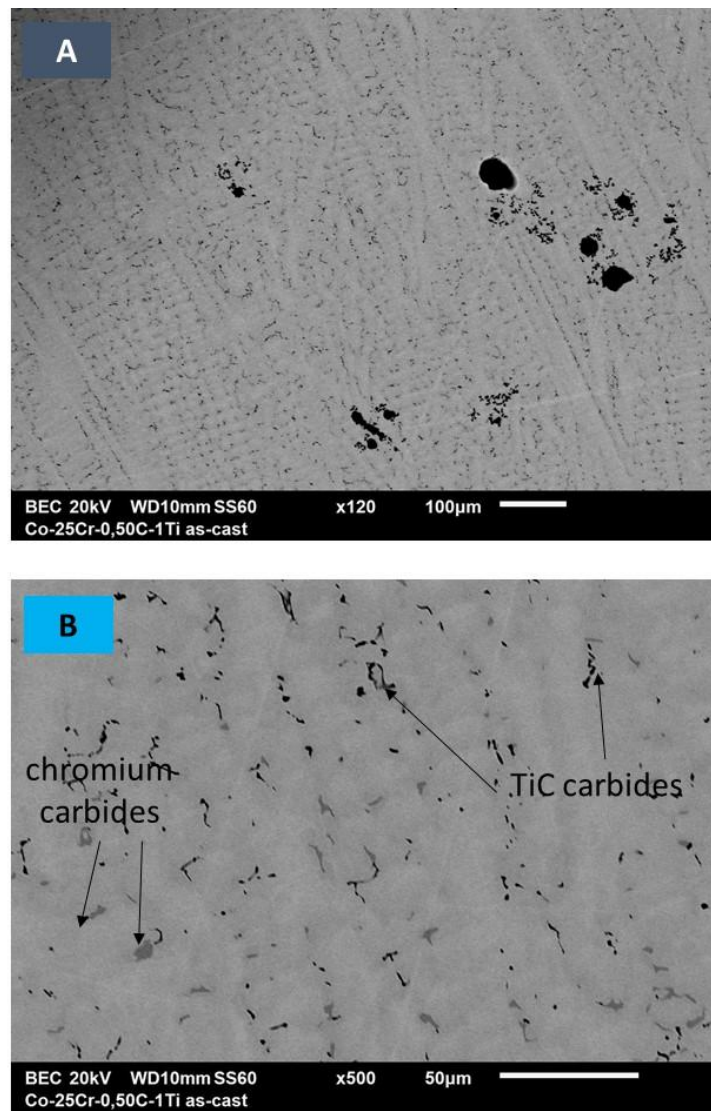


FIG. 2. General (A) et detailed (B) views of the as-cast Co-25Cr-0.50C-1Ti alloy (in wt%) when observed with the SEM in BSE mode.

TABLE 2. Chemical composition of the Co-25Cr-0.50C-1Ti alloy.

0.5C-1Ti	Co (wt%)	Cr (wt%)	Ti (wt%)
Average	73.27	25.87	0.86
SD	0.06	0.08	0.03

The third alloy, Co-25Cr-0.50C-2Ti, is also dendritic, and contains a lot of TiC carbides (FIG. 3A), the script-like morphology is more developed than in the two other alloys (FIG. 3B). Many coarse dark particles are also present. A few chromium carbides can be also noticed. Here too, the desired chemical composition was almost obtained (TABLE 3).

Spot EDS analysis was realized in several locations in the matrix to know the chemical composition of this phase. The results are given in TABLE 4. The main part of chromium is logically present in solid solution in the matrix of the alloys but several

weight per cent of this element is lacking, this can be explained by the presence of some chromium carbides. About 0.3 wt% in Ti is also present in the matrix for the 1 wt% Ti – containing alloys but almost three times this value is found in the matrix of the 2 wt% Ti – containing one. There is obviously more competition between chromium and titanium to form carbides than in Ta-containing or Hf-containing chromium-rich cobalt-based alloys, even if this is titanium which captures more carbon to form carbides.

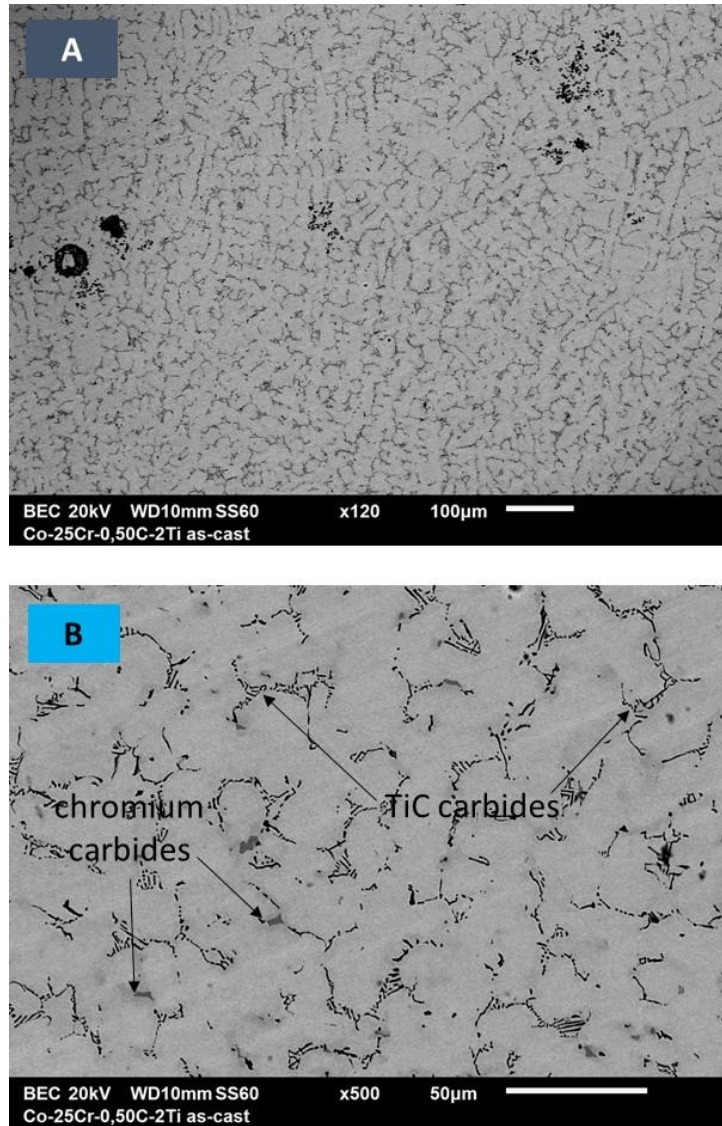


FIG. 3. General (A) et detailed (B) views of the as-cast Co-25Cr-0.50C-2Ti alloy (in wt%) when observed with the SEM in BSE mode.

TABLE 3. Chemical composition of the Co-25Cr-0.50C-2Ti alloy.

0.5C-2Ti	Co (wt%)	Cr (wt%)	Ti (wt%)
Average	72.31	25.82	1.87
SD	0.32	0.40	0.12

TABLE 4. The chemical compositions of the matrixes of the three alloys.

0.25C-1Ti	Co (wt%)	Cr (wt%)	Ti (wt%)
Average	73.60	25.59	0.83
SD	0.53	0.42	0.11
0.5C-1Ti	Co (wt%)	Cr (wt%)	Ti (wt%)
Average	73.27	25.87	0.86
SD	0.06	0.08	0.03
0.5C-2Ti	Co (wt%)	Cr (wt%)	Ti (wt%)
Average	72.31	25.82	1.87
SD	0.32	0.40	0.12

Despite their small sizes or thin shapes spot EDS analyses were also attempted on the dark particles. The results are given in TABLE 5 and 6. It can be seen that it was difficult to specify the chemical composition of the particles alone. Because of their small size the interaction pear included a part of the matrix, with as results significant contents in cobalt and chromium. Nevertheless, the high contents in Ti together with carbon, carbon and nitrogen, or with oxygen, demonstrate the presence of titanium carbides, titanium carbo-nitrides and sometimes of titanium oxide.

TABLE 5. Spot EDS analysis on the carbides (Co-25Cr-0.25C-1Ti alloy).

0.25C-1Ti	Co (wt%)	Cr (wt%)	Ti (wt%)	C (wt%)	O (wt%)	N (wt%)
TiC	50.47	25.81	16.55	7.17	-	-
Ti(C,N)	40.54	15.54	30.10	6.80	0.48	6.53
Ti(C,N)	49.63	17.10	18.44	3.62	-	11.21
TiN	29.37	11.40	39.31	1.03	-	18.89

TABLE 6. Spot EDS analysis on the carbides (Co-25Cr-0.5C-1Ti alloy).

0.5C-1Ti	Co (wt%)	Cr (wt%)	Ti (wt%)	C (wt%)	O (wt%)	N (wt%)
TiC	50.47	25.81	16.55	7.17	-	-
Ti(C,N)	46.28	18.87	25.78	5.97	0.06	3.04
TiN	24.49	9.61	44.10	2.06	0.74	19.01
TiN	29.37	11.40	39.31	1.03	-	18.89
TiO ₂	0.66	1.54	62.72	1.17	31.47	2.43

The obtained values of hardness (Vickers method, load: 10 kg) are given in TABLE 7. The values are all rather high (300HV₁₀ Kg and more) thanks to the intrinsic hard character of cobalt and of the presence of carbides. But a double population of carbides (alloys with 0.5 wt% C instead 0.25 wt% C) leads to the additional 60 Hv to 70 Hv.

TABLE 7. Results of Vickers indentations (10 tests/alloy, load 10 kg).

Alloy	Co-25Cr-0.25C-1Ti	Co-25Cr-0.50C-1Ti	Co-25Cr-0.50C-2Ti
Average	306	372	364
SD	21	40	12

Discussion

Titanium appeared as a stronger carbide-forming element than chromium. Titanium carbides were essentially obtained, although the content in chromium was much higher than the titanium one. Titanium plays in a {Co-25 wt% Cr}-base, the same role as tantalum, niobium, hafnium or zirconium by favoring the appearance at solidification of MC carbides instead chromium carbides. Some of the latter were seemingly observed, with morphology among the usual ones for such carbides when appeared at solidification [1-3]. However none of the spot analysis showed high concentrations in Cr.As TaC, NbC, HfC and ZrC the morphology of the Titanium carbides is of the script-type, as previously reported in several works [20,21] located in the interdendritic spaces and imbricated with matrix. This is probably favorable to high creep resistance at elevated temperature as previously observed for the other MC carbides. Some of the particles are also titanium carbo-nitrides and even titanium nitrides, maybe with the same script-like morphology, but the nature of these particles may influence, maybe in the wrong direction, the strengthening efficiency. These nitrides and carbo-nitrides, as well as the titanium oxides which were also observed, resulted from the reaction of Ti with the traces in N₂ and O₂ present in the used argon gas in which heating and melting were achieved during the elaboration of the alloys.

Conclusions

The presence of interdendritic script-like MC carbides was obviously successfully obtained in these cast chromium-rich cobalt-based alloys for a M element being titanium instead tantalum, niobium, hafnium or zirconium. However the high tendency of this element to react with oxygen and nitrogen lead to the presence, together with the wished TiC carbides, to Ti(C,N) carbo-nitrides and even TiN nitrides the effect of which on the mechanical properties can be detrimental for the mechanical properties. This merits to be verified soon. The stability of the TiC carbides at high temperature, in terms of volume fraction and of morphology must also be tested by long time exposures at elevated temperature, as well as the probable influence of all these particles on the high temperature behavior. Work is being carried out to get information in these fields.

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