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Microstructure and hardness of a low-chromium cobalt-based alloy reinforced by tantalum carbides destined to chromium pack-cementation

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ABSTRACT

Low chromium contents allow obtaining improved refractoriness in alloys, the chromia-forming behaviour of which being kept thanks to later Cr pack-cementation treatment on surface. The purpose of this work is to explore the microstructure of a {tantalum carbides}-reinforced cobalt-based alloys the bulk chromium content of which is particularly low to maximize its refractoriness and then its potential of creep-resistance. Thermodynamic calculations were first performed to study the theoretic microstructures at high temperature and to assess the gain in solidus temperature which can be expected by lowering the chromium content. A real alloy with 0.3 wt.%C, 5 wt.%Ta only 5 wt.%Cr was then elaborated by induction foundry in inert atmosphere, for examining its microstructure and to evaluating its machinability by measuring its macro- and micro-hardness. The as-cast microstructure shows a double-phased state: matrix and eutectic tantalum carbides, the later ones having kept a script-like morphology known to be favourable to high strength at high temperature. A rather high level of hardness is also kept, but a little decreased by comparison with same earlier studied cobalt alloys with 30 wt.%Cr. No chromium carbides able to perturb the pack-cementation were seen in the microstructure.

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KEYWORDS

Cobalt alloy;
Tantalum carbides;
Low chromium;
Thermodynamic calculations;
Hardness

INTRODUCTION

Chromium is the main element added to superalloys which are designed, not only to be resistant against dry corrosion by hot gases^[1,2], but also to efficiently resist corrosion by molten substances as molten salts, CMAS deposits or industrial molten glasses during their forming for finally obtaining insulation products, for in-

stance. Thus, chromium is present in cast superalloys with contents as high as about 30 wt.%, as encountered in most of glass forming tools made of nickel-based^[3] or cobalt-based^[4] carbides-strengthened cast superalloys. Unfortunately such high chromium contents tend to diminish the refractoriness of such alloys by comparison to Cr-poorer or Cr-free alloys of same composition concerning the other alloying elements. This

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can be illustrated in TABLE 1 which clearly shows the dependence of both liquidus temperature and solidus temperature on the chromium content for a TaC-containing cobalt-based alloy. Indeed the liquidus and solidus temperatures both decrease when the chromium content increases from 10 (a too low value to allow a chromia-forming behaviour in high temperature oxidation situation) to 30 wt.% (as generally required for the same purpose), even if the solidification scenario is not changed (start with FCC precipitation and end with the {matrix+TaC}-eutectic solidification). It can be mentioned that the decrease in chromium, which thus improves the alloy refractoriness, should additionally influence the mechanical behaviour by slightly decreasing the TaC volume fraction but also by probably slightly improving the solid solution strengthening (more tantalum in solution in the matrix at high temperature).

Despite that the natures, volume fractions and morphologies of the reinforcing phases of the carbides-strengthened cast superalloys are of prior importance, a high refractoriness is also generally required to achieve high mechanical properties at very high temperatures. The solidus temperature or fusion start temperature is demanded to be as high as possible, what can be obtained by optimizing the chemical composition of the

alloy. Decreasing the chromium content of the bulk may appear being a possible way to achieve such result, even if this implies that additional enrichment in chromium of the surface and sub-surface must be done to maintain at a level high enough the oxidation and corrosion resistances of the alloy at high temperature. It was earlier seen that such sub-surface chromium – enrichment was possible simply by pack-cementation for cobalt-based alloys and superalloys but by respecting specific conditions for the microstructures of the alloys, more precisely concerning the carbides natures^[5-7].

The purpose of the present work is to consider a simple cobalt alloy containing the same tantalum and carbon contents which allow obtaining in some high performance superalloys a sufficiently developed interdendritic network made of tantalum carbides to ensure high creep strength at high temperature, and to study the consequences on both microstructure and machinability, of a significant decrease in chromium content of its bulk: down to 5wt.%, a very low chromium content allowing later a successful Cr-enrichment by pack-cementation. This will be done first by preliminary thermodynamic calculations, and second by really elaborating the alloy and characterizing its microstructure and hardness.

TABLE 1: Evolution of the melting range of a Co-10Ni-xCr-0.4C-6Ta (all contents in wt.%) when the chromium content x increases from 10 to 30 w.%; present phases and matrix compositions at the temperatures of liquidus and solidus (all results according to Thermo-Calc)

Co-10Ni-xCr-0.4C-6Ta alloy		x (wt.%Cr)		
		10	20	30
T _{liq}		1415.95°C	1392.51°C	1363.57°C
Liquidus	Solid phase appearing first	FCC matrix (79.36Co – 9.68Ni-9.51Cr-1.37Ta-0.074C)	FCC matrix (69.94Co-9.79Ni-19.23Cr-0.98Ta-0.052C)	FCC matrix (60.35Co-9.95Ni-28.93Cr-0.73C-0.035C)
T _{sol}		1335.26°C	1307.65°C	1277.43°C
Solidus	Solid phases present (%.mass)	96.60% FCC matrix (76.18Co-10.35Ni-10.34Cr-2.94Ta-0.193C) 3.40% TaC	95.59% FCC matrix (55.33Co-10.32Ni-21.92Cr-1.97Ta-0.129C) 4.42% TaC	94.88% FCC matrix (56.49Co-10.54Ni-31.60Cr-1.28Ta-0.085C) 5.12% TaC
Microstructures at 1200°C		95.68% FCC matrix (76.92Co-10.45Ni-10.43Cr-2.06Ta-0.134C) 4.32% Ta	95.04% FCC matrix (66.92Co-10.52Ni-21.02Cr-1.44Ta-0.093C) 4.97% Ta	94.58% FCC matrix (56.67Co-10.57Ni-31.70Cr-0.99Ta-0.070C) 5.42% TaC
Microstructures at 1000°C		94.66% FCC matrix (77.75Co-10.56Ni-10.54Cr-1.08Ta-0.067C) 5.34% TaC	94.29 FCC matrix (67.45 Co-10.61Ni-21.19Cr-0.70Ta-0.044C) 5.72TaC	93.80 FCC matrix (57.08Co-10.66Ni-31.53Cr-0.71Ta-0.019C) 5.69% TaC & 0.51% M ₂₃ C ₆

EXPERIMENTAL

The alloy which was considered in this work had the targeted chemical composition: Co(bal.)-5Cr-0.3C-5Ta, all contents being expressed in weight percents. The study started by preliminary thermodynamic calculations to better know the metallurgical environment/neighborhood of this composition, more precisely to see the possible microstructures able to appear in case of content discard of carbon or chromium, and to explore the theoretic microstructure evolution of this alloy with temperature. Such calculations were performed using the Thermo-Calc version N software^[8] and a database which initially contained the descriptions of the Co-Cr-C system and its sub-systems^[9-14] but which was enriched by the description of the binary and ternary sub-systems Ta-C, Co-Ta, Cr-Ta and Co-Ta-C^[15-18].

The alloy was also really elaborated by foundry, using a CELES high frequency induction furnace working at about 110kHz and 4kV under a 300bars argon atmosphere to avoid any oxidation during the heating of the mix of pure metals (Alfa Aesar, purity > 99.9wt.%), their melting and solidification (all performed in the same water-cooled copper crucible of the furnace). The alloy was then cut, embedded in a cold resin mixture (manufacturer ESCIL: resin CY230 + hardener HY956), and then polished with SiC papers from 240 to 1200 grit, with final polishing done using a textile disk containing 1µm alumina particles, until obtaining a mirror-like surface state.

The chemical composition was controlled by Wavelength Dispersion Spectrometry (WDS) using a CAMECA SX100 microprobe with which electronic microstructures micrographs were taken. These micrographs were analysed using the Adobe Photoshop CS software in order to quantify the surface or volume fractions of the present phases. They were converted in mass fractions by using the following volume masses of the possible phases if present^[19]: 8.9 g cm⁻³ for the matrix, 6.94 g cm⁻³ for the Cr₇C₃ carbides and 14.5 g cm⁻³ for the TaC carbides.

Vickers indentations were performed using a Testwell Wolpert apparatus under a load of 30kg for obtaining values of macro-hardness, while a Reichert model D32 apparatus (load 32g) was additionally used for studying the heterogeneity of micro-hardness due to the double {metallic matrix + eutectic carbides} con-

stitution of the alloy.

RESULTS AND DISCUSSION

Preliminary thermodynamic calculations

Calculations were performed with Thermo-Calc to obtain a mapping in the {C: 0 to 0.5 wt.%C} × {T: 900

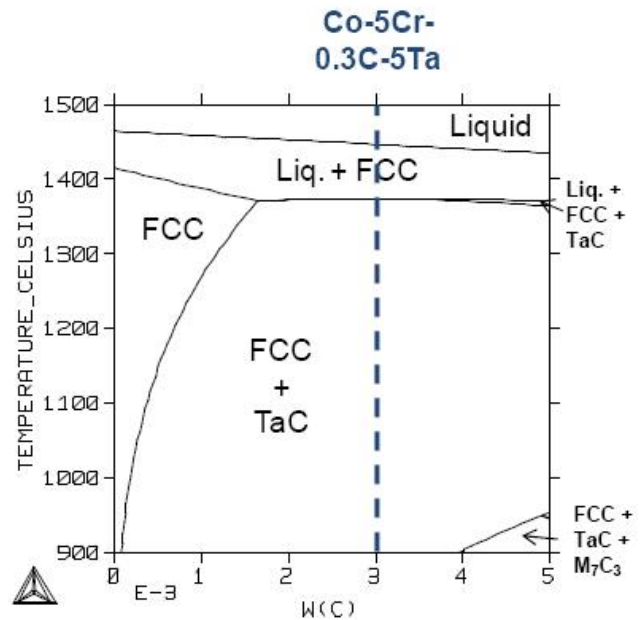


Figure 1 : Isoleth section at 5wt.%Cr of the Co-C-Ta-Cr phase diagram computed with Thermo-Calc; position and neighbourhood of the studied alloy

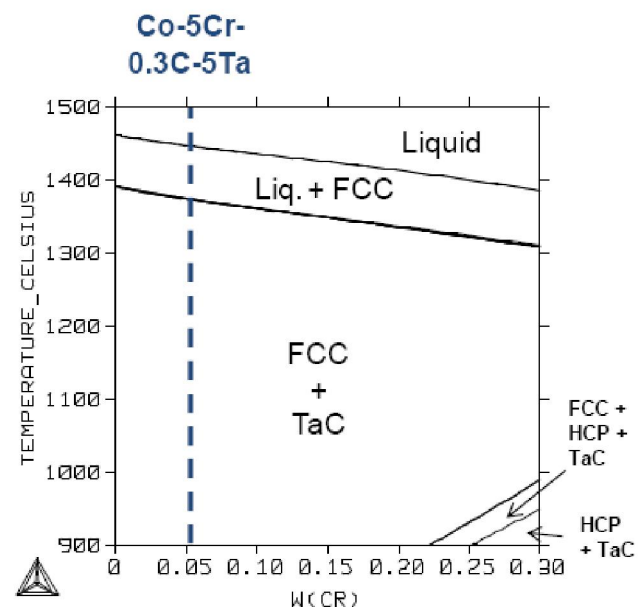


Figure 2 : Isoleth section at 0.3wt.%C of the Co-C-Ta-Cr phase diagram computed with Thermo-Calc; position and neighbourhood of the studied alloy

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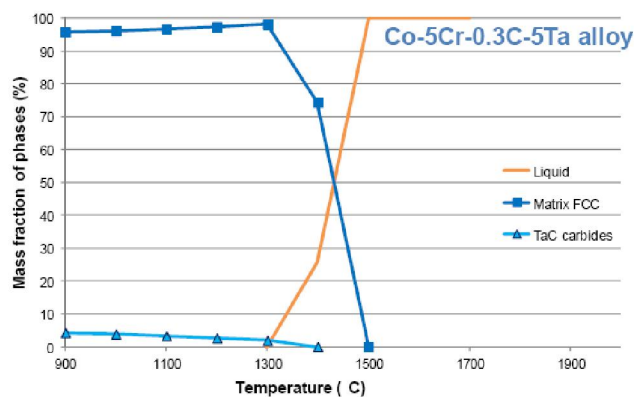


Figure 3 : Evolution of the phases natures and volume fractions during solidification and solid state cooling down to 900°C, according to Thermo-Calc

to 1500°C} area (Figure 1) in which the studied Co-5Cr-0.3C-5Ta is positioned. It appears, for the chosen chromium content, that the small variations in carbon content would induce neither qualitative change of the alloy microstructure at any of high operating temperature (this one ought to always remain FCC + TaC), nor significant change in solidus temperature (and in liquidus temperature).

Additional calculation mapping {Cr: 0 to 30 wt.%Cr} × {T: 900 to 1500°C} area was also performed with Thermo-Calc to observe the possible consequences of chromium variation around the targeted

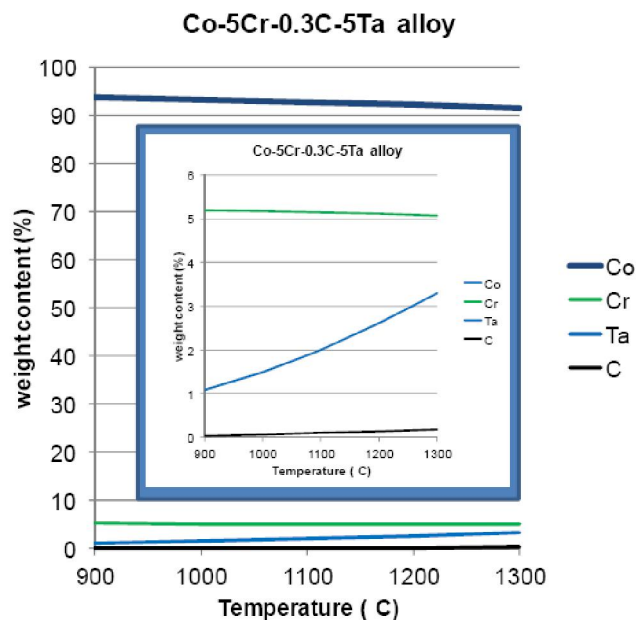


Figure 4 : Evolution of the chemical composition of the FCC matrix versus temperature (main graph: all elements including cobalt, inserted graph: enlarged view of the contents in elements present in low quantities)

value of 5 wt.%Cr (Figure 2). Here too a possible modification in chromium should only slightly change the mass fractions of the phases, but without qualitative change in this high temperature range. Furthermore, this figure graphically illustrates the gain in solidus temperature as well as in liquidus temperature by decreasing the chromium content: almost 100°C can be won by a decreasing from 30 wt.% Cr down to 0 wt.%.

The quantitative variations of the microstructure versus temperature, according to Thermo-Calc, are graphically represented in Figure 3 (mass fractions of phases) and in Figure 4 (chemical composition of the austenitic matrix: general and enlarged view inserted). One can see that the volume fraction of the tantalum carbide increases when temperature decreases, while the contents in tantalum and carbon both decrease in the same time.

Chemical composition, microstructure and hardness of the alloy really elaborated

Because of not-melted small parts the chemical composition of the main part of the alloy is (3.71 wt.%Cr; 4.61 wt.%Ta) against the targeted values (5 wt.% Cr; 5 wt.% Ta), while the carbon content cannot be determined with this technique (too light element and too low targeted content). These values, which did not respect the targeted ones, are not fortunately not too far from what was initially desired.

The microstructure of the obtained alloy is illustrated in Figure 5 with a micrograph taken using the microprobe. The alloy is composed of a dendritic matrix {Co(bal.) - 4.25±0.07 wt.% Cr - 1.52±0.17 wt.% Ta} with a composition not too far from the calculated one (5.19 wt.% Cr and 1.08 wt.% Cr for 900°C), considering that it cannot be known at which temperature the chemical composition of matrix finished during the cooling.

The microstructures were analysed to assess the surface fractions of carbides. The results obtained from four areas of about 0.1 mm² led to 9.59 ± 0.99 surf.% of tantalum carbides (white particles), which can be converted in 14.73 ± 1.42 mass.%. These values are significantly higher than the ones predicted by Thermo-Calc. This mismatch can be attributed to the fact that the calculated mass fractions are the theoretic ones corresponding to a chosen temperature in the thermody-

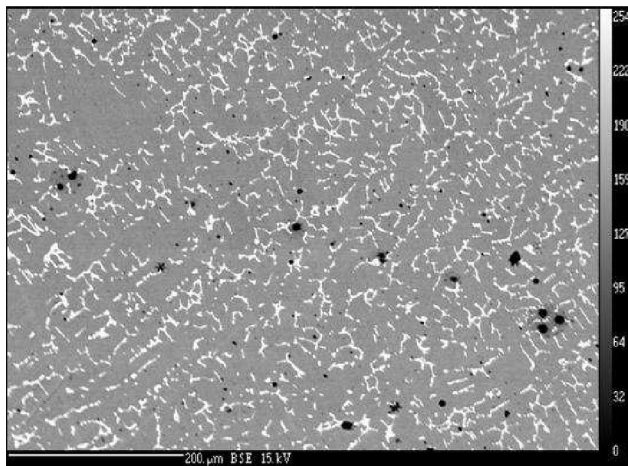


Figure 5 : Microstructure of the main part of the alloy

dynamic stable state while the mass fractions issued from the measured ones on the real alloy do not correspond to any thermodynamic stable state.

The Vickers hardness of the alloy was determined by macro- and micro-indentation. The results are presented in TABLE 2. The macro-hardness is about 30 Hv30kg lower than the one of a Co-30Cr-0.3C-4.2Ta elaborated following the same route and earlier studied^[20]. This can be due to the lowest matrix hardening

TABLE 2 : Values of macro- and micro-hardness

HARDNESS 30kg (whole alloy)	Hardness 32g matrix	Hardness 32g interdendritic spaces
325	290	335
±13	±7	±17

by solid solution, consequence of the much lower chromium content. The hardness distribution in the microstructure is heterogeneous since it varies between areas of lower hardness (matrix) and areas of higher hardness (eutectic containing carbides).

General commentaries

The decrease in chromium content from the usual 30 wt.%, value generally considered as compulsory to keep a chromia-forming behaviour for the resistance against dry oxidation and corrosion at high temperature if the alloy is not protected to the aggressive fluid medias by a coating, down to 5 wt.% Cr, leads to a jump in refractoriness of more than 60°C: solidus temperature rise from 1307.87 (i.e. 1310°C) to 1373.86°C (i.e. 1375°C) as determined by Thermo-Calc). Such gain in refractoriness is to consider as a probable good point for the creep resistance. Unfortunately, at the same

time, the liquidus temperature rises from 1385.08 (i.e. 1385°C) to 1446.92°C (i.e. 1445°C) which may cause technical problem for fusion and the pouring techniques. Beside these computed data (theoretic since a real alloy is often not really at a thermodynamic stable state), the real synthesis of an alloy allowed observing that the fractions of strengthening carbides may be higher than predicted (but unfortunately also that the initial carbides may evolve to lower fractions in service at high temperature) but also that, about what thermodynamic calculations with the tool used here is not able to give some information, the morphology of the carbides issued from solidification are suitable for a mechanical reinforcement at high temperature especially efficient (script eutectic carbides). These are two (similar volume fractions and morphologies) of the reasons why the room temperature hardness is of the same order of magnitude of TaC-reinforced 30 wt.%Cr-containing cobalt-based superalloys actually really in service. It is nevertheless true that the hardness is slightly lower because of a matrix not so rich in chromium atoms hardening the matrix in solid solution (for about the same quantity of tantalum atoms present in solid solution).

No other carbides than the tantalum carbides were clearly seen in the microstructure of the Cr-poor cobalt alloy. This is a point on which one must keep an eye since, if really present in the microstructure at the beginning of a chromium pack-cementation process, chromium carbides may be destabilised and then dissolve. Thereafter the C atoms delivered by these carbon reservoirs may diffuse towards the surface where the chromium activity is especially high. In such situation an external scale of chromium carbide (Cr_7C_3 for example) may develop and thicken instead a real chromium enrichment in sub-surface. This scenario, which earlier happened in Co-Cr-C alloys poor in chromium and tantalum-free, but also in Co-Cr-C-Ta alloys in which tantalum was present in quantities no high enough to obtain exclusively tantalum carbides, was in contrast avoided when the tantalum carbide – much more stable than chromium carbides – was the single carbon-rich phase present. But one can think that such condition is not always sufficient since matrix may itself contain not too low carbon quantities in solid solution, as illustrated in Figure 4.

CONCLUSIONS

Low-chromium aluminium-free cobalt alloys are intrinsically poor in the field of the resistance against oxidation and corrosion at high temperature but they can be considered as potentially high-temperature mechanically strong bulk alloys destined to be subjected to surface treatment devoted to the hot chemical aggressions. Indeed, refractoriness is considerably increased by the minimization of the bulk chromium content while the strengthening tantalum carbides are still present, with furthermore a favourable morphology. However the pack-cementation parameters for the chromium subsurface enrichment have to be carefully rated to optimize this chromium inward diffusion to obtain a sufficiently deep chromium enriched zone to minimize the risk of eventual crack propagation to internal zone too poor in chromium and then threatened by catastrophic oxidation.

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