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Behaviour at high temperature of two cobalt-based superalloys reinforced by carbides. Part 2: Case of a medium carbon {Co-0.6C-23.5Cr-10Ni-3.5Ta-7W}-based superalloy

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ABSTRACT

This second part of the work concerns the fine microstructure version of the second alloy out of the two complex carbide-strengthened cast cobalt-based alloys elaborated in laboratory. This second alloy, also synthesized by melting of pure elements and solidification in fast cooling conditions was here too subjected to high temperature oxidation for its surface and subsurface, and high temperature exposure for its bulk. The same temperatures and durations as in the first part were applied: 1050 and 1150°C, 66 and 146 hours. In contrast with the first studied alloy the high temperature oxidation behaviour of this second alloy was generally good, characterized by the appearance and sustainability of an outer covering chromia scale protecting the alloy. Catastrophic oxidation only occurred in some rare locations for the most severe conditions (the highest temperature and longest duration). The bulk microstructure evolved during these tests - a general coarsening of all carbides - with as consequences a decrease in room temperature hardness suggesting a weakening of the mechanical resistance at high temperature, similarly to what was observed for the first alloy.

KEYWORDS

Commercial Co-based superalloy;
High temperature microstructure;
Hot oxidation;
Room temperature hardness.

INTRODUCTION

As already reminded in the first part of this work[1] the cast equiaxed cobalt-based superalloys represent high temperature materials solutions which remain rather cheap - and not too difficult to elaborate - solutions for many applications concerned by hot conditions of working. Indeed, they stay interesting combinations of, on the one hand high potential of resistance against hot oxidation and corrosion with the high quantities of chromium that they usually contain[2], and on the other hand high potential of resistance against static stress or creep deformation with the presence of primary and/or secondary carbides which can be present in high quantities[3]. The two commercial Co-based superalloys Mar-M 322 and Mar-M 509 are well-known representative examples of this family[4]. These alloys were recently subjected to elaboration at the laboratory scale

in conditions of fast cooling[5] in order to better know the as-cast microstructures to which such conditions may lead. Since the microstructure fineness of alloys may have great influence on the high temperature oxidation behaviour of carbides-strengthened alloys and superalloys[6,7], the study of the hot oxidation phenomena occurring for these finely microstructure alloys was undertaken first with the high carbon CoX alloy[1], with additionally an eye on the possible bulk microstructure evolution.

In this second part, the second alloy - the medium carbon CoY one representing the Mar-M 509 commercial superalloy - the as-cast microstructure and room temperature hardness of which were already respectively described and measured in a recent work[5], was also exposed to laboratory air at two different high temperatures (1050°C and 1150°C) and for a rather short duration (66 hours) and a longer one (146 hours), here too to observe how this fine microstructure alloy behaves in the field of oxidation as well as in the one of microstructure stability.

EXPERIMENTAL

The alloy under study

Let us reminding that the alloy CoY was synthesized in laboratory by High Frequency induction melting under inert atmosphere[5]. The targeted chemical composition was the one of the commercial Mar-M 509 alloy: Co(bal.)-23.5Cr-10Ni-0.6C-3.5Ta-0.2Ti-7W-0.5Zr, while the chemical composition really obtained was the following one*: Co(bal.)-24.11Cr-10.29Ni-0.6**C-4.04Ta-0.04Ti-7.36W-0.25Zr (*: technique used: Energy Dispersion Spectrometry; **: cannot be measured because too light element, content supposed to be respected). The obtained as-cast microstructure – illustrated by a micrograph in Figure 0 (left) - is composed of a dendritic matrix of cobalt solid solution and of an interdendritic network of M_7C_3 and MC carbides. The latter ones contained tantalum but also tungsten and titanium. In the same figure, on the right, there is a graph representing the development of the microstructure of the CoY alloy according to thermodynamic calculations performed with the Thermo-Calc software[8]. For these calculations a database issued from the SSOL one[9] (already containing the descriptions of the Co-Cr-C systems and its sub-systems[10-15]) was enriched with new systems' descriptions[16-18] for improving the previsions of MC-type carbides.

One can see that, in contrast with the CoX alloy for which MC carbides crystallized first, it is here the cobalt-based austenitic matrix of the CoY alloy which should appear as single solid phase at the beginning of solidification. About fifty degrees bellow, the MC carbides would start crystallizing and develop more or less simultaneously with the last part of matrix. At the end of solidification some M_7C_3 chromium carbides would also

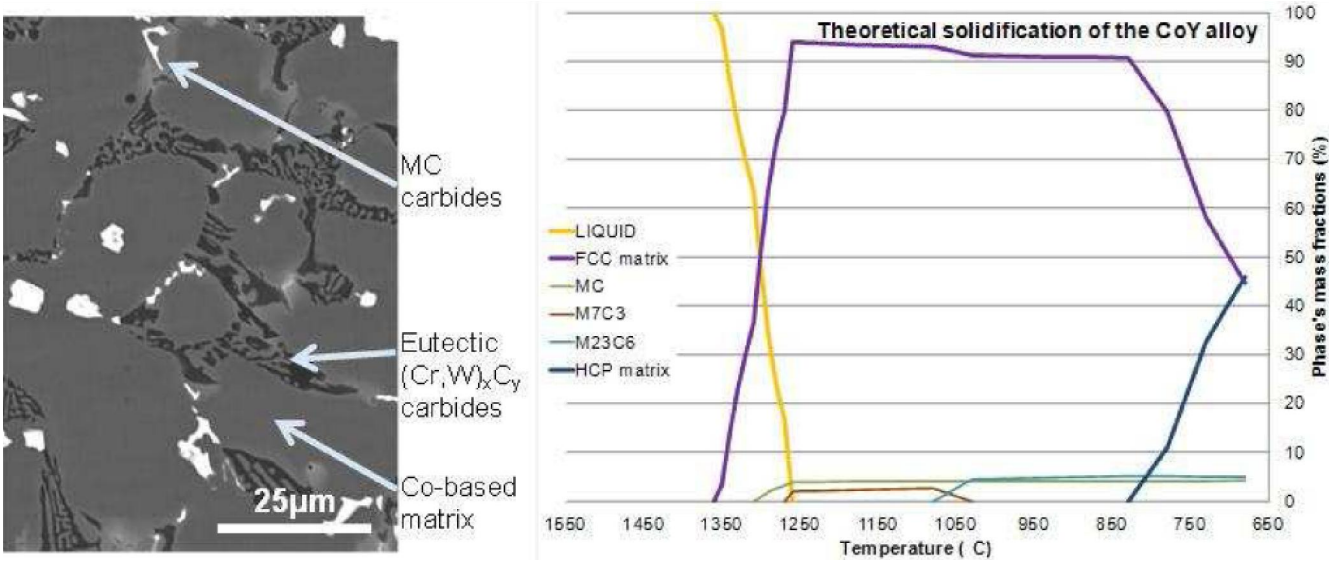


Figure 0 : Micrograph (Scanning Electron Microscope in Back Scattered Electrons mode) of the as-cast microstructure of the CoY alloy (left side) and theoretic solidification sequences plotted from Thermo-Calc calculations' results (on the right)

appear. Under 1100°C these M_7C_3 carbides would transform into $M_{23}C_6$ carbides, over a short range of temperatures (centred on 1050°C) and, for lower temperatures (under 850°C) the austenitic Face Centred Cubic (FCC) matrix should be progressively replaced by its Hexagonal Compact Phase allotropic form.

Thus the MC carbides, and especially the chromium carbides, would be eutectic carbides, what should be in good agreement with their morphologies. The CoY alloy is then a cobalt-base alloy containing in its interdendritic spaces eutectic carbides, of chromium and of tantalum (and of the other MC-forming elements present in the composition).

High temperature tests, metallographic preparation and observations; hardness measurements

As for the CoX alloy of the first part of this study, four about 100mm^3 samples were cut in the ingot for the high temperature exposures. Their two main faces were polished with 1200-grit SiC papers and placed in an alumina nacelle inside the resistive tubular furnace Carbolite. The same parameters of heating, dwell and cooling as for the CoX alloy were applied: heating at 10°C min^{-1}, dwell at 1050°C and 1150°C for 66 hours and 146 hours, cooling in furnace after shutting off.

The oxidized samples were covered with a thick layer of electrolytic nickel, cut, embedded in a cold resin, and polished (SiC papers from 120 or 240 up to 1200 under water, 1µm-particles enriched textile disk) until obtaining a mirror-like surface state.

The observation/characterization of bulk, sub-surface and external oxides were done using a JEOL JSM 6010LA Scanning Electron Microscope (SEM), in Back Scattered Electrons (BSE) mode and at different magnifications. The Energy Dispersive Spectrometry (EDS) device equipping the SEM allowed specifying the different present oxides in the external scales and in the subsurfaces. EDS pinpoint measurements were performed to obtain inward concentration profiles from the extreme surface. Three micrographs were taken in BSE mode in the bulk to be analyzed with the image analysis tool of the Photoshop CS software of Adobe, for obtaining the surface fractions of the different types of carbides.

Indentations were here too performed to obtain Vickers hardness values for comparison with the results obtained for the as-cast alloy. The same apparatus (Testwell Wolpert) was used, with a load of 30 kg again, for obtaining three values to calculate the average hardness and standard deviation.

RESULTS AND DISCUSSION

General aspect of the alloys after oxidation tests

Macrographs of the samples oxidized during 66h or 146h at 1050°C or 1150°C are given in Figure 1 (one or two pictures when both sides were scanned). As previously seen with the CoX alloy it is already visible on these macrographs that the CoY alloy was logically more oxidized for a higher temperature for a same duration and for a longer duration at a given temperature. Oxidation seems having been significantly stronger at 1150°C, notably when the duration was the longest (146h).

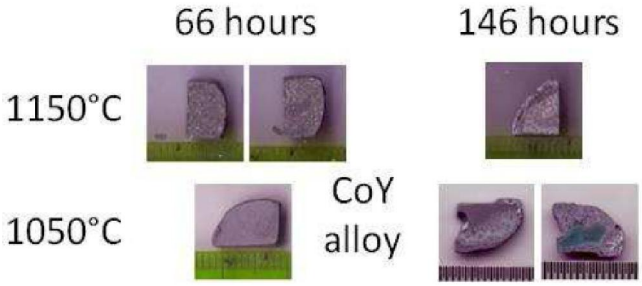


Figure 1 : Scanned images of the oxidized samples (scanned)

Surfaces and sub-surfaces: characteristics of the oxides formed and chemical modifications in the alloy

Micrographs of the oxidized surface and deteriorated subsurface of the four oxidized samples are given in Figure 2 (CoY alloy after 66h at 1050°C), Figure 3 (after 146h at 1050°C), Figure 4 (after 66h at 1150°C) and Figure 5 (after 146h at 1150°C) for illustrating the surface and sub-surfaces states after the four oxidation runs. One can see that, in the three first cases the CoY behaved as chromia-forming since a continuous protective Cr_2O_3 scale (identified by EDS pinpoint measurement) existed over the main faces of the samples after high temperature oxidation. This is in good agreement with the still rather high chromium contents (also measured by EDS) in extreme surface: between 14 and 15 wt.%Cr globally for the two durations at 1050°C and slightly more than 13 wt.% for 66 hours at 1150°C.

In the last case, e.i. after 146 hours of oxidation at 1150°C, the surface state is heterogeneous since some surface locations are still protected by an external chromia layer (chromium content in extreme surface near

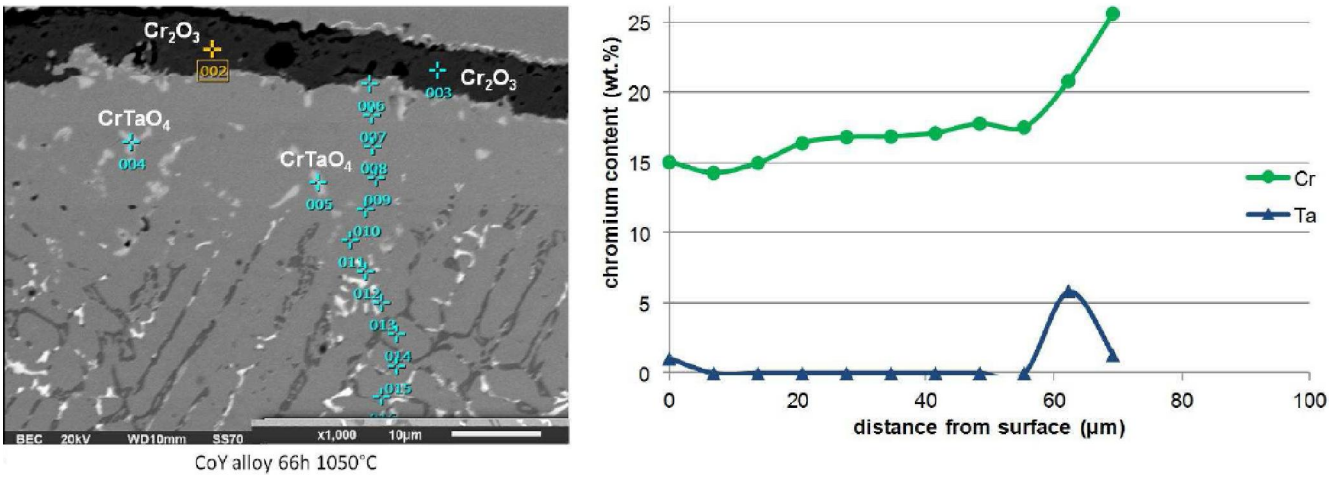


Figure 2 : Micrograph of the surface and subsurface of the CoY alloy oxidized during 66h at 1050°C, with identification of the different oxides and the concentration profile (of the Cr and Ta only) acquired on the points marked on the micrograph

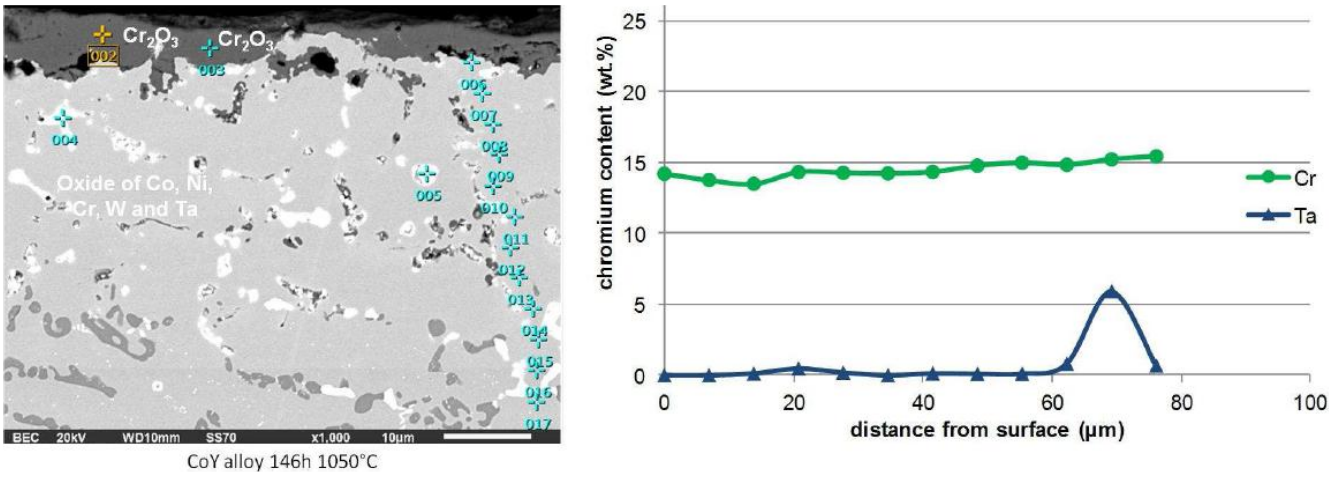


Figure 3 : Micrograph of the surface and subsurface of the CoY alloy oxidized during 146h at 1050°C, with identification of the different oxides and the concentration profile (of the Cr and Ta only) acquired on the points marked on the micrograph

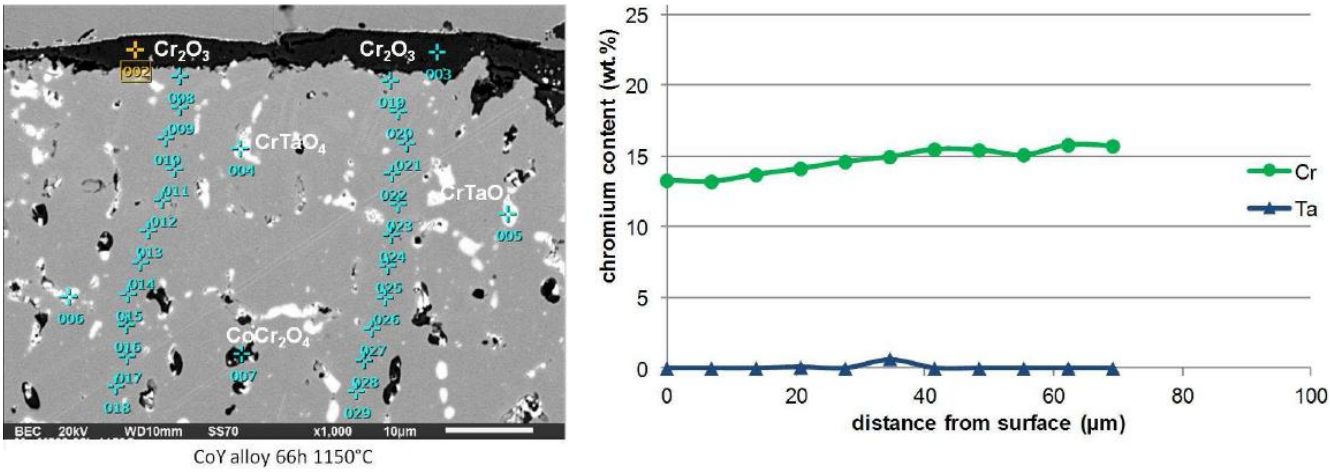


Figure 4 : Micrograph of the surface and subsurface of the CoY alloy oxidized during 66h at 1150°C, with identification of the different oxides and the concentration profile (of the Cr and Ta only) acquired on the points marked on the micrograph

14wt.%) while other locations have begun catastrophic oxidation: locally thick oxides containing not only chromia and $CrTaO_4$, but also the spinel $CoCr_2O_4$ for example (and chromium contents in extreme surface decreased down to 10 wt.%). In all cases internal oxidation also occurred with principally $CrTaO_4$ islands in the carbide-free zone.

Bulk microstructures after high temperature exposures; new values of hardness

The changes affecting the carbides were, for the sub-surface, their disappearance from the extreme surface over an increasing depth (causing the inward development of a carbide-free zone), and for the alloy core some modifications of natures, surface fractions and morphologies (Figure 6: after 66 and 146 hours at 1050°C, Figure 7: after 66 and 146 hours at 1150°C). After 66 hours at 1050°C one can notice a slight coarsening of the carbides, a little more accentuated after 146 hours at the same temperature (with possible precipitation of secondary carbides during the dwell or during the subsequent slow cooling). After exposure at 1150°C, during 66 hours and 146 hours, this carbide coarsening phenomenon is more obvious, notably for the chromium carbides which have totally lost their acicular shape.

There are also changes in volume fractions, assumed to be close to the surface ones which were measured by image analysis. The evolution with time (0h: as-cast, 66h and 146h) for the two levels of temperature (1050 and 1150°C) are graphically presented in Figure 8. The chromium carbides, which had surface fractions initially three times higher than the MC carbides (in the as-cast condition), seem evolving in surface fraction but not significantly by considering the uncertainty bars. What can be however considered as sure is the decrease observed after 146 hours at 1150°C, with final fractions significantly lower than after 146h at 1050°C, than after 66h at 1150°C and than as-cast. In contrast, by taking also into consideration the uncertainty bars, the surface fraction of the MC carbides does not vary significantly: it obviously depends neither on the aging temperature, nor on the aging duration.

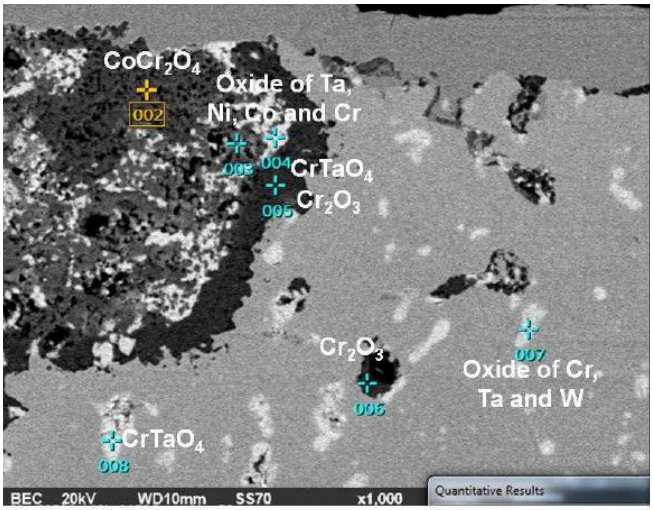
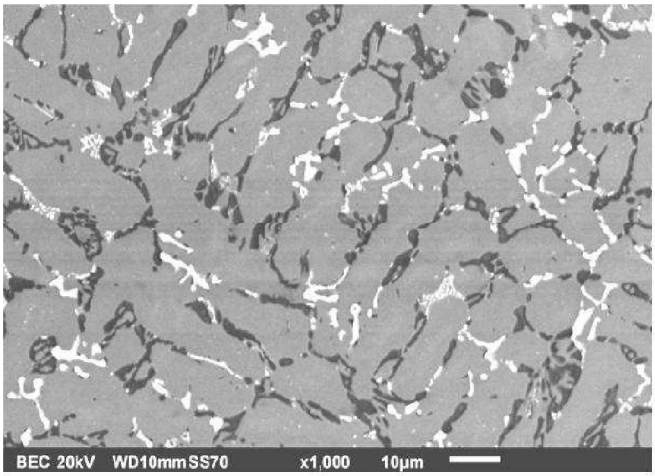


Figure 5 : Micrograph of the surface and subsurface of the CoY alloy oxidized during 146h at 1150°C, with identification of the different oxides



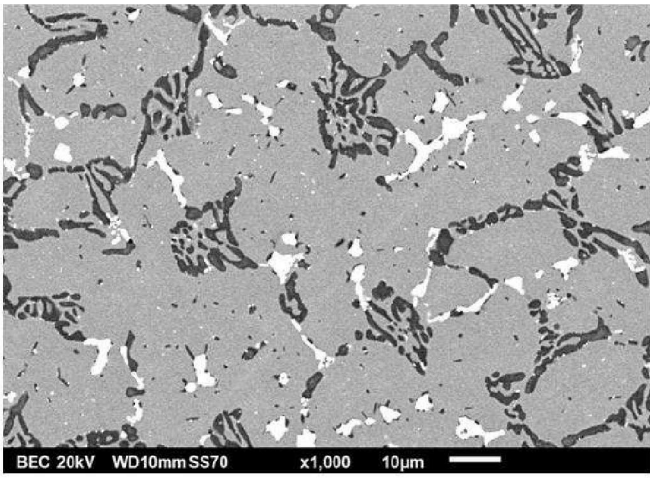


Figure 6 : Micrographs illustrating the bulk microstructure of the studied CoY alloy after exposure at 1050°C during 66h (left) and during 146h (right); white MC carbides and dark chromium carbides

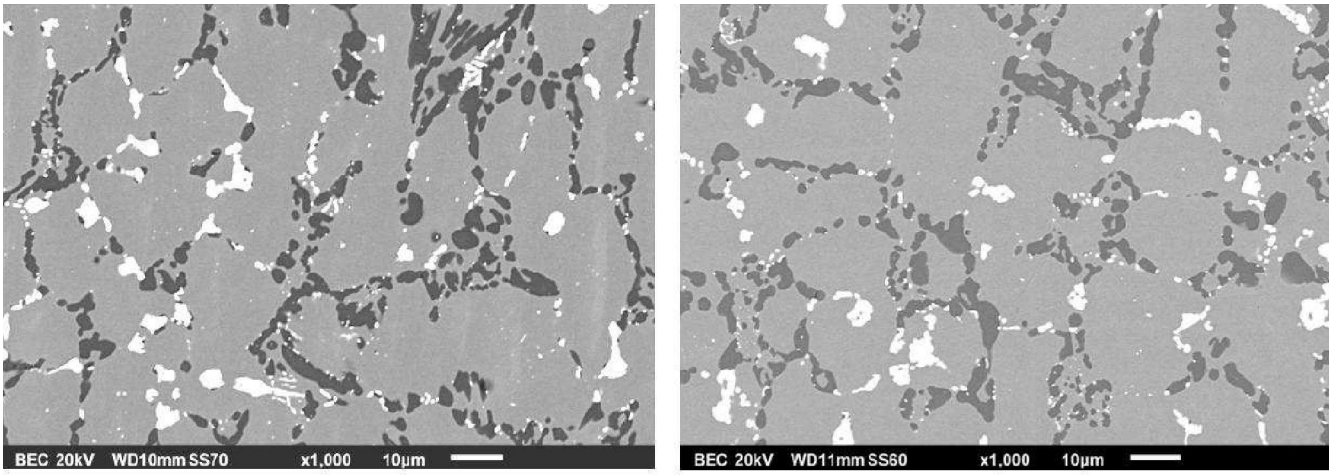


Figure 7 : Micrographs illustrating the bulk microstructure of the studied CoY alloy after exposure at 1150°C during 66h (left) and during 146h (right); white MC carbides and dark chromium carbides

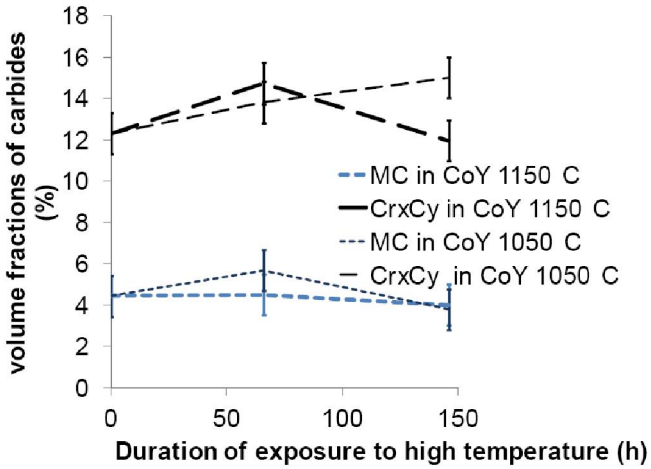


Figure 8 : Evolution of the carbide fractions of the CoY alloy with time for the two temperatures

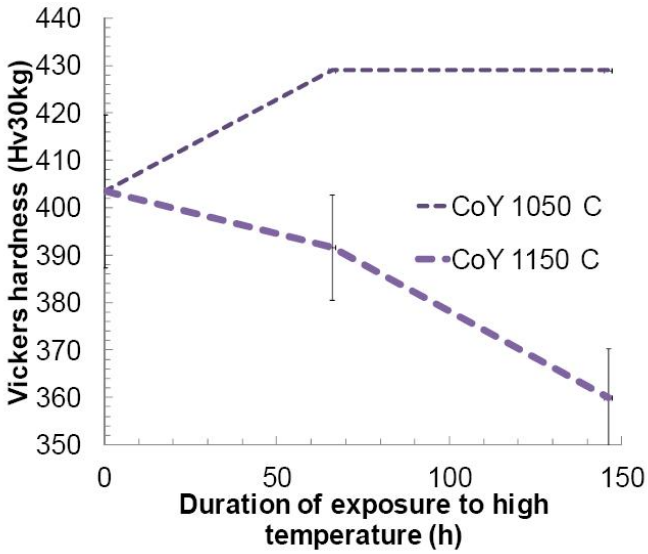


Figure 9 : Evolution of the hardness of the CoY alloy with the temperature and the duration of the exposure to high temperature

The hardness was measured three times per aged samples and the obtained average and standard deviation values are graphically given in Figure 9 in comparison with the as-cast ones. One can see that, after exposure to 1050°C, the hardness of the CoY alloy tends slightly increasing (after 146h at 1050°C, about 30Hv more than for the as-cast condition). The evolution with time spent at 1150°C is inverse: from as-cast to 66h at 1150°C and from 66h to 146h at the same temperature, the hardness progressively decreases, with a final loss of about 50Hv compared with the as-cast condition.

General commentaries

This second fine microstructure version of a commercial cobalt-based superalloy has thus shown a rather good resistance against hot oxidation. First the macro-aspects of the oxidized CoY samples were much better than the CoX ones, and second catastrophic oxidation only occurred for 146 hours at the temperature of 1150°C (very high for a cast cobalt-based alloy), moreover not for the whole surface but only in some locations. By comparison the CoX alloy was covered by a chromia scale, and then not too oxidized, only in the case 66hours – 1050°C. In addition, the extreme surface chromium contents, logically lowered during oxidation, were still at a rather high level (typically 15 wt.%) while much lower values were measured in the same

locations on the oxidized CoX samples. This difference of high temperature oxidation between the two alloys is to be found surely in the difference of chromium content (24.1 wt.% in CoY against only 22.3 wt.% in CoX, obtained/analyzed Cr contents) but maybe also in the better continuity of the interdendritic carbides network of CoY (easier diffusion of Cr towards the oxidation front) as well as possibly in the presence of slightly more than 10 wt.% Ni in the matrix (which may also facilitate a little Cr diffusion).

The hardness of the CoY alloy after return to room temperature was changed, for a higher value (case of 1050°C) or a significantly lower one (case of 1150°C, 146h). In the first case a solid state additional precipitation of carbides may be supposed (of chromium carbides notably: Figure 8) while the morphology change of the carbides - notably the chromium carbides (evident coarsening) - can be responsible of the relative softening observed after exposure to 1150°C. These observations, which well match with what was observed for the CoX alloy (same slight hardening and significant softening phenomena for 1050°C and 1150°C respectively), let thinking perhaps to a progressive slight strengthening of the alloy at 1050°C and more surely to a mechanical weakening at 1150°C. Always concerning hardness one can see that the values measured for the CoX alloy and the CoY one are very similar for the same aged conditions, despite the higher carbon content of the CoX alloy. The carbides of the CoY alloys, which were obviously more eutectic and interdendritic - and paradoxically more connected (by considering the lower carbon content of this CoY alloy by comparison with the CoX one) – were more favourable to high hardness, this allowing filling the hardness gap due to the difference in carbon content.

CONCLUSIONS

Thus, this CoY alloy, replicating the commercial Mar-M 509 alloy with a fine microstructure correctly behaved in high temperature oxidation, even at 1150°C which can be considered as a very high working temperature for a cast cobalt-based alloy. It is possible that the high density of interdendritic boundaries emerging per surface unit area, resulting from this microstructure fineness had played an important role in this good behaviour (greater easiness for chromium to diffuse and consequently maintain a chromia scale). This was not the case for the CoX alloy, which was a fine microstructure version of the first commercial superalloy Mar-M 322, may be because a general chemical composition with chromium content too low in its case. With their room temperature hardness of the same level one can extrapolate in a first time this similarity to high temperature mechanical properties, since the reinforcement by carbides seems equivalent. However the melting start temperatures are also to be taken into account, and furthermore the truth remains to be discovered by real mechanical tests at high temperature.

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