



Materials Science

An Indian Journal

Full Paper

MSAIJ, 10(2), 2014 [49-56]

High temperature oxidation of cobalt-based alloys strengthened by hafnium carbides Part 2: Metallography results

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ABSTRACT

The three cast HfC-strengthened cobalt based alloys previously tested in oxidation at 1200°C during 50 hours by recording mass gain were, in this second part of this work, metallographically characterized, as the two ternary chromium carbides – strengthened alloys introduced in the study for comparisons. X-Ray Diffraction runs and Energy Dispersion Spectrometry were performed to bring information concerning the constitution of the external oxides while SEM examinations allowed characterizing the microstructure changes in the bulk. None of the five alloys showed a chromia-forming behaviour as already suggested by the rather fast mass gains. The oxides are multi-constituted and notably contain cobalt oxides, spinel cobalt-chromium oxide, and sometimes hafnium oxide in the case of the HfC-strengthened alloys. In contrast with the ternary alloys that loosed all their carbides, the interdendritic HfC carbide network of the three Hf-containing alloys remained unchanged during the high temperature exposure. This demonstrates the interesting mechanical potential of such alloys for high temperatures application, but maybe also the necessity to improve their oxidation resistance, for example by increasing their chromium content or by applying a chromium rich coating.

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KEYWORDS

Cobalt-based alloys;
Hafnium carbides;
High temperature oxidation;
Post-mortem characterization.

INTRODUCTION

Hafnium is an element which is generally added to superalloys in rather low quantities, as for example 1.5 wt.%, 0.75 wt.% and 0.15 wt.% in the cast nickel-based alloys "Mar-M 247", "René 80 Hf" and "René N4" respectively. Hf is also present with contents equal to 1.5 wt.% in the cast cobalt-based alloys "B-1900 + Hf" and "Mar-M 200 + Hf"^[1]. What is generally expected is an improvement of the resistance of the alloys

against oxidation at high temperature^[2]. Hafnium is also a particularly strong carbide-former element and adding several weight percents of Hf to alloys already containing carbon leads to the development of a dense interdendritic network of eutectic HfC carbides during solidification. It has been observed earlier that such HfC carbides are much more stable in terms of volume fraction and morphologies than other MC carbides appeared in other alloys during solidification too^[3], what is probably favourable to a high level of mechanical

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resistance at high temperature maintained on long times. In contrast first results had earlier shown that the high temperature oxidation behaviours of alloys strengthened by interdendritic HfC carbides tend to be worse than alloys of the same base but containing chromium carbides or tantalum carbides instead hafnium carbides, for example in the case of cobalt alloys^[4]. This was here deeper studied in the case of cobalt alloys strengthened by HfC carbides with different carbide densities, previously elaborated and microstructurally characterized in their as-cast state^[5]. In the first part^[6] of the present work thermogravimetry runs were performed and the resulting mass gain files extensively exploited (isothermal part but also the heating part and cooling part). This already led to interesting observations, notably by comparison with chromium carbides – containing alloys with similar compositions except hafnium. In this second part the oxidized samples are metallographically prepared and characterized, in order to get additional information to exploit for a better understanding of the oxidation kinetic characteristics revealed for these alloys in the first part of this work.

EXPERIMENTAL DETAILS

Reminder of the details of the chemical compositions, elaboration and high temperature oxidation tests

Three HfC-strengthened Co-based alloys were elaborated from pure elements by High Frequency Induction melting under argon, then solidified in the cold crucible of the HF furnace with the form of 40g-weighting ingots. One can remind that the number of alloys under study is five:

- three Hf-containing ones: “Co-25Cr-0.25C-3.72Hf” (really containing 25.51wt.% Cr and 3.81wt.% Hf), “Co-25Cr-0.50C-3.72Hf” (really containing 25.59wt.% Cr and 3.88wt.% Hf) and “Co-25Cr-0.50C-7.44Hf” (really containing 25.82wt.% Cr and 8.78wt.% Hf),
- and two ternary alloys for comparisons: “Co-25Cr-0.25C” (really containing 24.22wt.% Cr) and “Co-25Cr-0.50C” (really containing 23.79wt.% Cr), with Co: bal. and C: not measured (all measured contents being issued from Energy Dispersion Spectrometry analysis).

In the centre of each of the five ingots a sample with a near parallelepipedic geometry was cut then polished (final polishing realized with 1200-grit SiC). The thermogravimetry runs were performed in artificial air using a Setaram TG92 thermobalance (heating rate: 20°C min⁻¹, isothermal stage: 50h at 1200°C, cooling rate: -5°C min⁻¹).

Post-mortem characterization of the oxidized samples

After oxidation test, the oxidized surfaces were analyzed in X-Ray Diffraction (Cu K_α: λ=1,5406 Angströms) using Philips X’Pert Pro diffractometer. Each oxidized sample was thereafter coated on both sides (main faces) by cathodic pulverization of gold (allowing the external oxide scales being electrically conductive on their external sides). This allowed thereafter depositing an electrolytic continuous (and thick enough) nickel layer by cathodic polarization in a heated (50°C) Watt’s bath, for preventing loss of the external oxides during cutting. Finally the fully coated samples were cut, embedded in a cold {resin + hardener} mixture (ESCIL), polished from 240-grit to 1200-grit SiC papers, ultrasonically cleaned and polished again, this time with a textile disk enriched with 1µm hard particles, until reaching a mirror-like surface state.

The surface states were examined with a Scanning Electron Microscope (SEM) JEOL JSM-6010LA essentially in Back Scattered Electrons (BSE) mode at different magnifications. Several pinpoint EDS measurements were performed for specifying the chemical compositions of the different present external oxides as well as the chemical composition of the alloy in its most external part.

RESULTS AND DISCUSSION

Analysis of the oxide external surface

As detected, in the first part of this work, on the cooling parts of the mass variation curves, the alloys have obviously suffered oxide spallation, with a more or less severe loss of the external oxide. Figure 1 presents the macrographs of one of the two main faces of each of the five samples under study. Notably, on the face photographed in the top-left corner in Figure 1 the whole external oxide has lost the Co-25Cr-0.25C-

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3.72Hf alloy.

Before cutting, electrolytic coating and embedding, the oxidized samples were analyzed by X-Ray Diffraction. The obtained results, illustrated in Figure 2 in the case of one of the two Hf-free alloys and in

Figure 3 in the case of one of the Hf-containing alloys, confirm first that the samples are partly denuded because of oxide spallation (peaks belonging to the alloy itself (fcc and hcp cobalt matrix) and second show that the oxides present on surface are multiple. Indeed, in addition to chromia (Cr_2O_3) one can notice the presence of cobalt oxide (mainly CoO and seemingly Co_3O_4 too) and of the spinel CoCr_2O_4 over the Hf-free ternary alloys. The same oxides are present over the Co-25Cr-0.50C-3.72Hf. In contrast, the cobalt oxides are absent while oxides of hafnium (HfO_2) are present in the scales covering the two other Hf-containing alloys, as HfO_2 . It seems, on the one hand that Hf, or the HfC carbides, are more exposed to oxidation when HfC is the single or almost single carbide present in the alloy, and on the other hand that the formation of HfO_2 oxides inhibits the formation of cobalt oxides.

Analysis of the oxide external oxide in cross-section

After electrolytic nickel deposition to prevent any additional loss of external oxide during cutting, the oxi-

dized samples were cut in two parts and embedded in resin, then polished for allowing cross-section observations. The oxides formed over the ternary alloys as well as over the Hf-containing ones are not homogeneous all around the cross-sections in terms of thickness as well as of natures. Indeed some locations have obviously suffered of catastrophic oxidation (thick multi-constituted local scales) while neighbour zones had not yet really fallen in a high oxidation rate. For the external oxides selected around the cross-sections EDS analysis confirmed the presence of at least cobalt oxides and of the spinel oxide of both cobalt and chromium over the ternary alloys (Figure 4 and Figure 5) while chromia was found for example on the surface of the oxidized Co-25Cr-0.25C-3.72Hf alloy (Figure 6). Additional pinpoint EDS measurements also show that the chromium content just under the alloy external surface has decreased from the initial 25 wt.% down to less than 19 wt.% and even locally down to less than 17 wt.%. Even if such values are not very low these decreases are significant enough to promote the loss of a chromia-forming behaviour for cobalt-based alloys, as this can be observed here. Indeed it is often considered that 30 wt.% of Cr is the limit in chromium content still allowing cobalt alloys to behave as chromia-forming alloys. The values measured here in the outer side of the sub-sur-

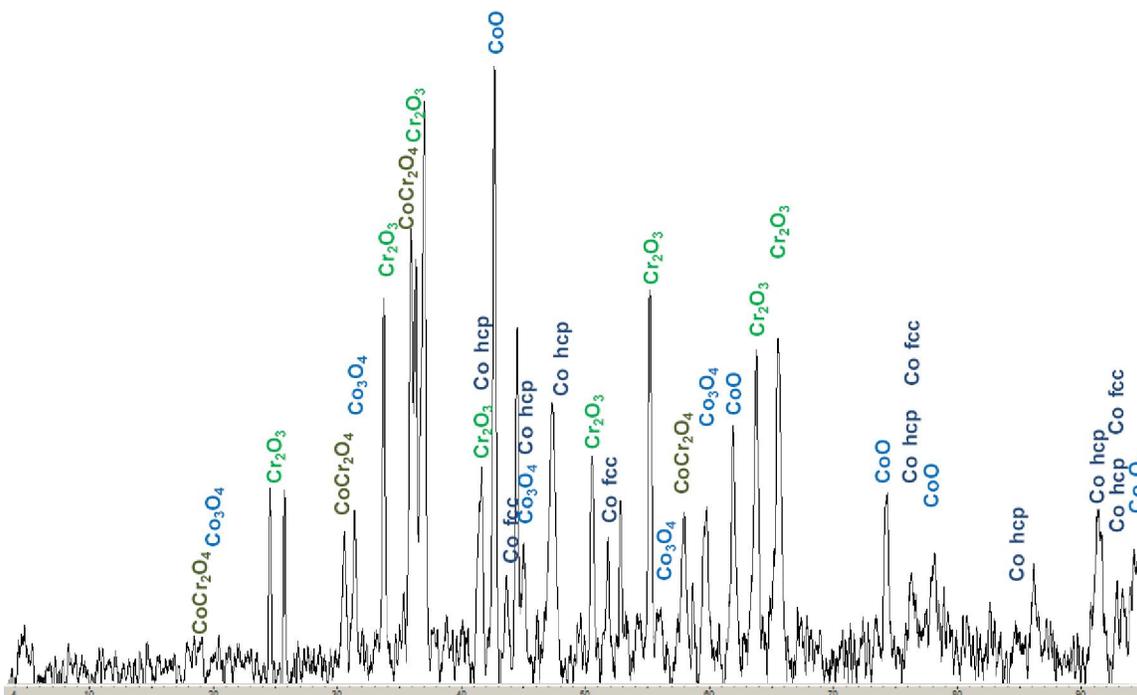


Figure 3 : XRD pattern acquired on the surface of the oxidized Co-25Cr-0.50C-3.72Hf ternary alloy

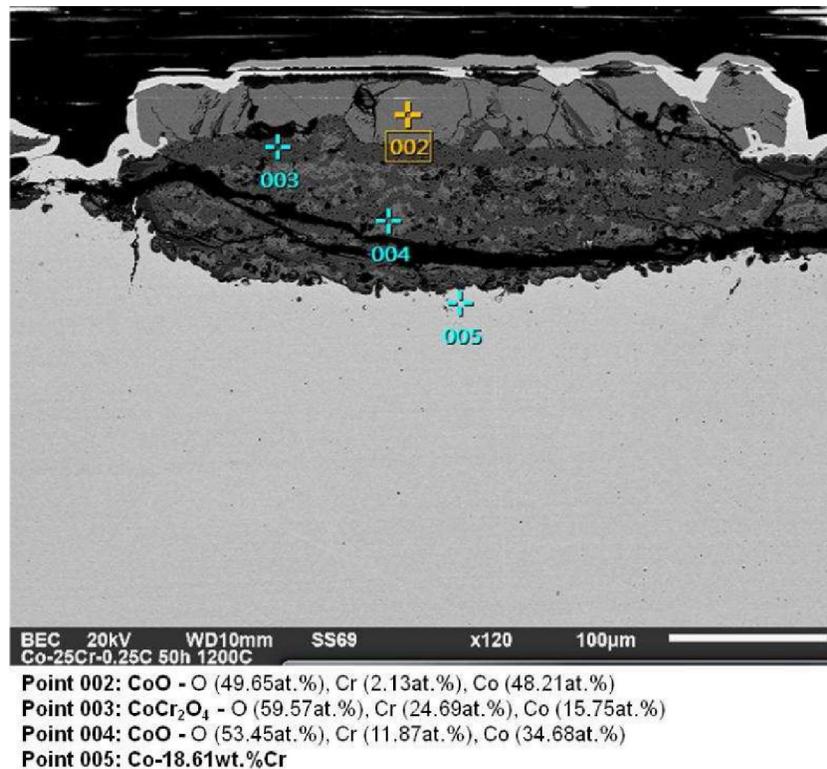


Figure 4 : EDS pattern analysis of parts of external oxides remained stuck to the surface of the one of the oxidized ternary alloys (Co-25Cr-0.25C)

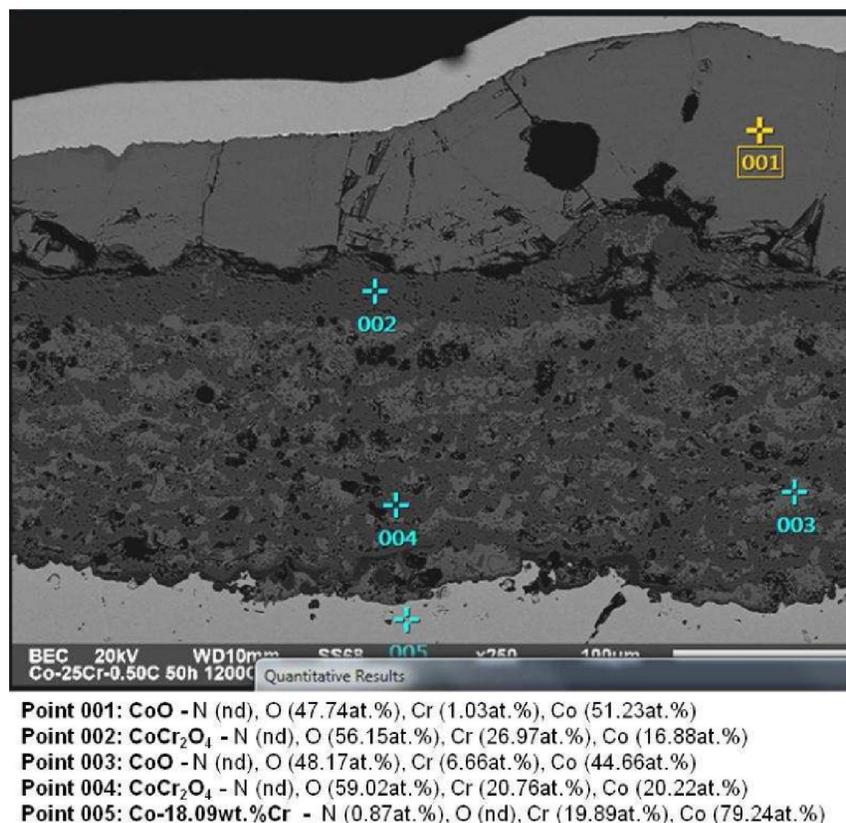


Figure 5 : EDS pattern analysis of parts of external oxides remained stuck to the surface of the other oxidized ternary alloy (Co-25Cr-0.50C)

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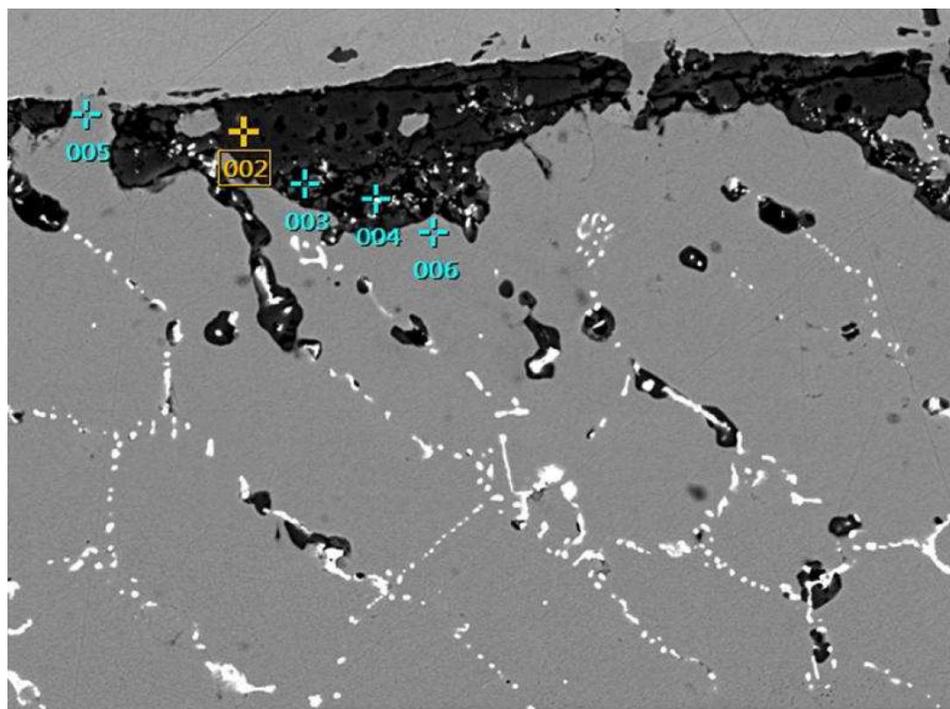
face, after 50 hours of oxidation at 1200°C (which is a rather high temperature for such alloys) are lowered enough to threaten the chromia-forming behaviour. One also must underline that the initial chromium content (25 wt.%) of all the alloys of this study was already lower than the 30 wt.%Cr.

Consequences of the oxidation on surface for the bulk microstructure

The bulk microstructures of the two ternary alloys after oxidation tests (heated samples) are presented in Figure 7 (the two bottom micrographs), while their initial microstructures are reminded in the two micrographs just above. All carbides seem have disappeared in the two bulk microstructures. Since the 0.25wt.%C-containing alloy was already very poor in carbides in the as-cast condition, it is not surprising that no carbides can be seen in the heated sample. In contrast the difference is much more visible in the case of the 0.50wt.%C-containing alloy since carbides, which were quite present

in the as-cast microstructure, are now totally absent in the bulk (in the heated state). This phenomenon, which obviously affected here the Co-25Cr-0.50C but probably too the Co-25Cr-0.25C even if the latter did not initially contain many carbides, was earlier observed^[7] for Co-30Cr- (0.2 to 0.8wt.%) C after also 50 hours of oxidation at 1200°C while, in the same previous study, carbides were still present in the bulk of these alloys after oxidation at 1000 and 1100°C. This carbides disappearance can be attributed to the rapid oxidation occurring at 1200°C, which drawn both the chromium and carbon atoms of the sample bulk, decreased the local chromium and carbon contents and destabilized the chromium carbides.

The Hf-containing alloys also underwent microstructure modifications of their bulk since the HfC carbides tended a little to become fragmented, coalesced and rounder than before. This is more detectable in the 3.72wt.%Hf-containing alloy (Figure 8 top) than in the 7.44wt.%Hf-containing one. In the two cases the de-



Point 002: Cr₂O₃ - N (nd), O (59.86at. %), Cr (38.42at. %), Co (1.68at. %), Hf (0.03at. %)
Point 003: Cr₂O₃ - N (nd), O (47.44at. %), Cr (51.14at. %), Co (0.61at. %), Hf (0.81at. %)
Point 004: Cr₂O₃ - N (nd), O (69.58at. %), Cr (27.86at. %), Co (0.96at. %), Hf (1.61at. %)
Point 005: Co-15.21wt.%Cr - N (4.22at. %), O (0.53at. %), Cr (16.29at. %), Co (78.96at. %), Hf (nd)
Point 006: Co-16.67wt.%Cr - N (1.90at. %), O (nd), Cr (18.22at. %), Co (79.88at. %), Hf

Figure 6 : EDS pattern analysis of parts of external oxides remained stuck to the surface of the one of the oxidized ternary alloys (Co-25Cr-0.25C-3.72Hf)

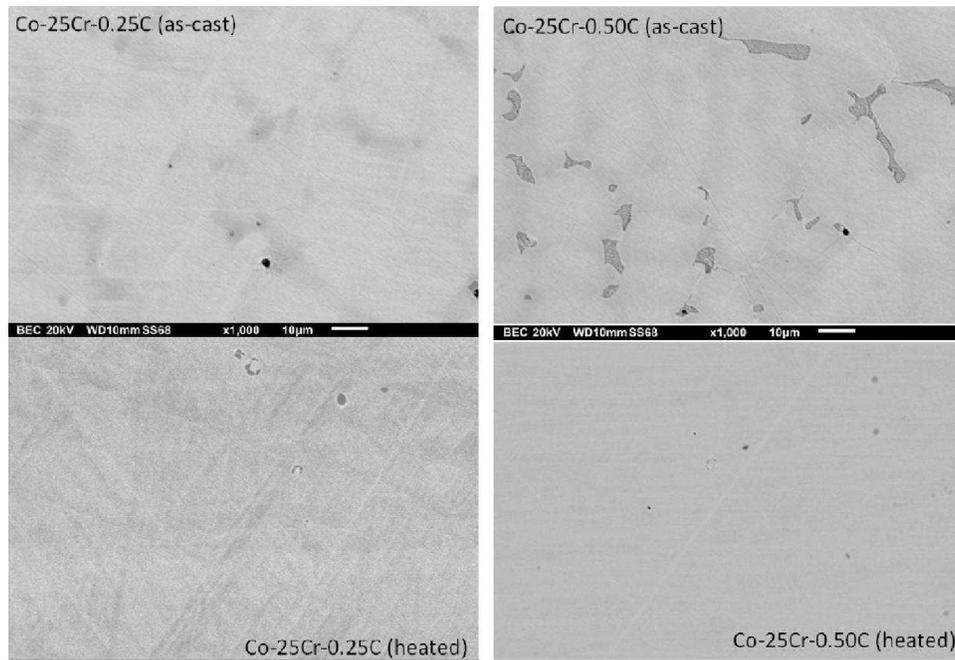


Figure 7 : Bulk microstructure before and after high temperature oxidation for the two Hf-free ternary alloys

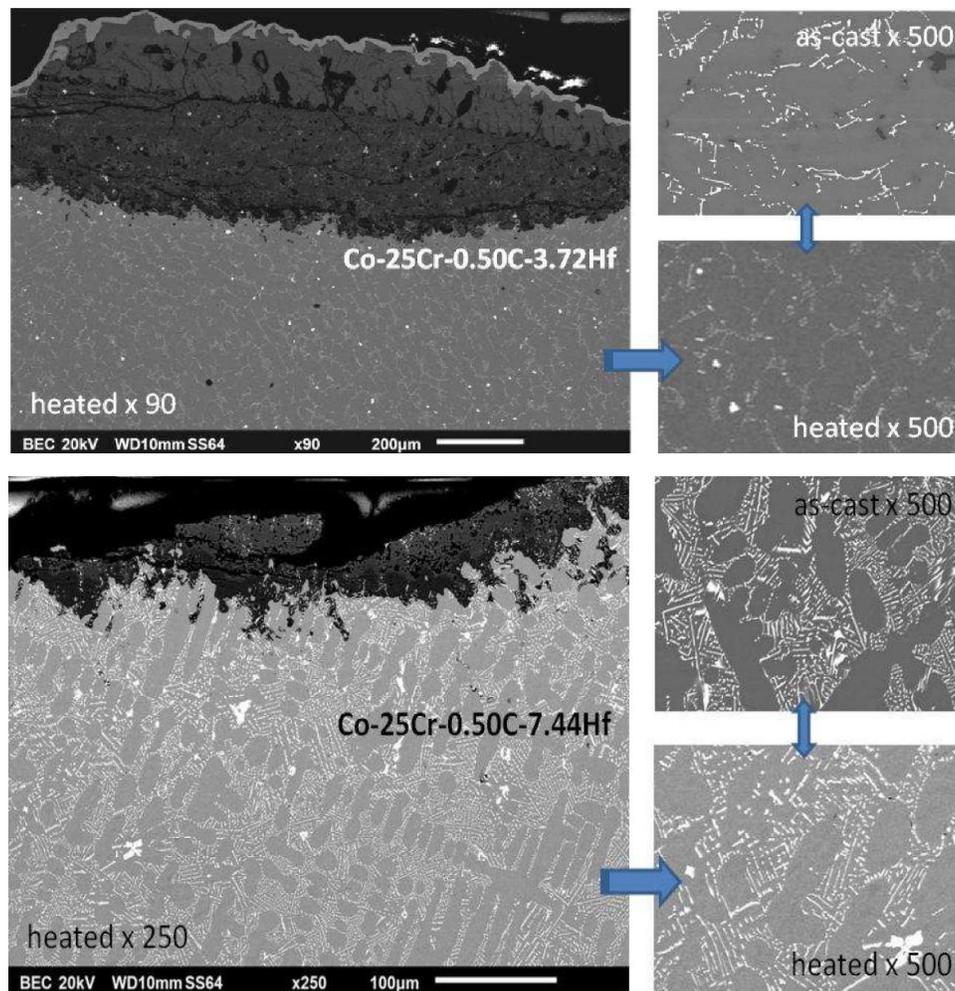


Figure 8 : Bulk microstructure before and after high temperature oxidation for two of the Hf-containing quaternary alloys

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terioration of the carbide network is much more limited than in previously studied TaC-strengthened alloys^[4,8].

General commentaries

The metallographic examinations of the oxidized samples complete the kinetic results presented in the first part of this work.^[6] As characterized by X-Ray Diffraction analysis and by SEM/EDS examinations/chemical measurements, before cutting and after cross-section preparation respectively, the external oxide thickness developed on surface during the thermogravimetry tests are more (Hf-containing alloys) or less (Hf-free ternary alloys) homogeneous, while the nature of this oxide is, in all cases, rather complex.

Over the surfaces of the Hf-free-ternary alloys the oxides of cobalt (CoO, Co₃O₄) as well as the spinel CoCr₂O₄ oxide are present instead only chromia, in some locations the fast oxidation of which is obviously responsible of the loss of the slow parabolic kinetic partly replaced by an almost linear faster mass gain. This also induced the disappearance of the chromium carbides initially present in the bulk.

In the cases of the three Hf-containing alloys, the kinetic, which tended to remain parabolic, was especially fast. The multi-constituted oxide – containing chromia but also the spinel CoCr₂O₄ oxide and cobalt-oxide – thickened rapidly, leading to a very thick oxide which induced during cooling the enormous mass loss when the spallation, a little delayed by the presence of hafnium, finished to occur. One can remark that HfO₂ formed in the external scales in the case of the two alloys containing mainly or exclusively HfC carbides, obviously obstructing the formation of cobalt oxides. However, in contrast with the ternary alloys (loss of all carbides, e.i. maximal carbide-free zone, extended to the sample center), the carbides initially present in the Hf-containing alloys were almost not affected neither by the oxidation phenomena (notably: no carbide-free zone) nor by the rather long (50 hours) exposure to very high temperature (1200°C).

CONCLUSIONS

The 25wt.%Cr-containing HfC-strengthened cobalt-based alloys studied in this work exhibit a resistance against oxidation which is not perfect, probably due to their rather low Cr contents but maybe also to the presence of so

high hafnium quantities. Indeed their behaviour at 1200°C are characterized by a fast – but parabolic – mass gain and by multi-constituted external oxide scales – instead pure chromia - not favourable to a slow oxidation. However, the interdendritic carbide network did not suffer of the long time exposure at high temperature, in contrast with the chromium carbides of the ternary alloys studied for comparison. Such alloys need to be improved in their oxidation behaviour to allow exploiting their high temperature potential, for example by enriching their surface and sub-surface in chromium by pack-cementation for example, a Chemical Vapour Deposition technique which allowed significantly increasing the oxidation resistance of chromium-poor cobalt-based alloys^[9-11].

ACKNOWLEDGEMENTS

The authors wish thanking very much Miss Elodie CONRATH who performed the thermogravimetry runs.

REFERENCES

- [1] M.J.Donachie, S.J.Donachie; Superalloys: A Technical Guide, 2nd Edition, ASM International, Materials Park, (2002).
- [2] J.Young; High temperature oxidation and corrosion of metals, Elsevier, Amsterdam, (2008).
- [3] P.Berthod; Journal of Alloys and Compounds, **481**, 746 (2009).
- [4] P.Berthod; Annales de Chimie – Science des Matériaux, **34(5)**, 275 (2009).
- [5] P.Berthod; Materials Science: An Indian Journal, in press.
- [6] P.Berthod, E.Conrath; Materials Science: An Indian Journal, submitted.
- [7] P.Berthod; Annales de Chimie – Sciences des Matériaux, **33(3)**, 247 (2008).
- [8] P.Berthod, C.Heil, L.Aranda; Journal of Alloys and Compounds, **504**, 243 (2010).
- [9] G.Michel, P.Berthod, M.Vilasi, S.Mathieu, P.Steinmetz; Surface and Coatings Technology, **205**, 3708 (2011).
- [10] G.Michel, P.Berthod, M.Vilasi, S.Mathieu, P.Steinmetz; Surface and Coatings Technology, **205**, 5241 (2011).
- [11] G.Michel, P.Berthod, S.Mathieu, M.Vilasi, P.Steinmetz; The Open Corrosion Journal, **4**, 27 (2011).