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Influence of the water vapour content in air on the high temperature oxidation of cobalt-based alloys part 2: results in wet air

Patrice Berthod[1,2,3]*, Lionel Aranda[3], Thierry Schweitzer[3], Alexandre Navet[4], Albert Leroy[4]
[1]University of Lorraine, (FRANCE)
[2]Faculty of Sciences and Technologies, (FRANCE)
[3]Institut Jean Lamour (UMR 7198), Team 206 “Surface and Interface, Chemical Reactivity of Materials”
B.P. 70239, 54506 Vandoeuvre-lès-Nancy, (FRANCE)
[4]Lycée Henri Loritz, 29 rue des Jardiniers, 54000 Nancy, (FRANCE)
E-mail: Patrice.Berthod@univ-lorraine.fr

ABSTRACT

This second part of the work carried out on the possible influence of water vapour in air on the high temperature oxidation of chromium-rich cobalt-based alloys presents the results obtained for their exposure during 46 hours at 1000, 1100 and 1200°C in 10%H_2O –containing air. Post-mortem characterization of the nine samples oxidized in wet air was carried out and the results compared to the ones obtained in dry air and already presented in the first part. The oxide scale spallation tended to be more severe here in wet air, notably for the carbide-free Co-10Ni-30Cr alloy. No significant differences were seen for the two other alloys. The first observations of the external fineness and morphology of the oxide scale did not reveal fundamental differences. The single point of interest was the chromium on extreme surface which were almost systematically higher after oxidation in wet air than in dry air. Future work is envisaged with higher water vapour content expecting to enhance the possible effect of water vapour.

KEYWORDS

Cobalt alloys;
Water vapour;
High temperature oxidation;
Tests in wet air;
Metallography characterization.

INTRODUCTION

The applications involving high temperature of service in oxidative atmospheres are often concerned by the additional presence of more or less water vapour[1-3]. When present gaseous H_2O co-exists with the most common gaseous oxidant specie – O_2 – but also, in more complex hot atmospheres, with N_2[4], H_2[5,6], CO[7,8] or HCl[9], for example. For the refractory alloys and superalloys the presence of water vapour is not neutral for their sustainability since this may influence their behaviour in oxidation at high temperature, and then their deterioration rate and finally the lifetime of the components which are made with these alloys. This is the reason why many alloys were studied in oxidation in various water vapour containing gases, among them many steels and nickel-based alloys. In contrast, the high temperature oxidation behaviour of cobalt-based superalloys – another important family of high temperature alloys – in contact with atmospheres containing water vapour was much less studied.

In this second part of the work, the first part of which dealt with oxidation tests carried out in dry air for preparing comparisons, the high temperature oxidation behaviours - in presence of water vapour - of the same three cobalt-based alloys under interest were explored for the same thermal cycles, including notably the 46 hours stages at 1000, 1100 and 1200°C.

EXPERIMENTAL

Recall of the characteristics of the alloys and sample's preparation

These three alloys, a ternary one Co(bal.)-10wt.%Ni-30wt.%Cr, a quaternary one Co(bal.)-10wt.%Ni-30wt.%Cr-0.5wt.%C, and a quinary one Co(bal.)-10wt.%Ni-30wt.%Cr-0.5wt.%C-7.5wt.%Ta, were chosen to represent an important part of the chromia-forming cobalt-based superalloys' family. For that the first one was wished as carbide-free, the second one as strengthened by chromium carbides, and the third one by tantalum carbides (all carbides being primary and inter-dendritic). They were elaborated by High Frequency induction from pure elements under inert atmosphere and their solidification took place in a water-cooled copper crucible. The obtained rather fast solidification rate led to rather fine microstructures but meeting the initial microstructural requirements above. Their microstructures are already illustrated and described in the first part of this study[10].

Among the six parallelepiped samples (7 mm × 7 mm × 2 mm, all around ground with 1200-grit SiC-paper initially prepared for the oxidation tests, the three first ones were already used in oxidation by dry air[10]. The three other were still available for the present tests in wet air.

Oxidation tests, metallographic preparation and post-mortem characterization

The samples were exposed to a flow of synthetic air (80%N_2-20%O_2) enriched with water vapour (90% air – 10% H_2O) in the hot zone of a tubular resistive furnace (Carbolite). They underwent a heating at +20K min^{-1} up to 1000, 1100 or 1200°C, temperature at which they stayed during 46 hours before the cooling which was done at -5 K min^{-1}. After return to ambient temperature the oxidized samples were scanned with a simple office scanner to get macrographs, then covered with a thin gold deposited by cathodic pulverization which allows the external oxide scale observations in electron microscopy. The second role of the gold deposition, giving electrical conductivity of the oxidized samples, was to allow the electrolytic deposition of nickel all around the oxidized samples immersed in a heated Watt's bath. The thick Ni layer allowed thereafter protecting the scales during the cutting in two parts which were embedded and ground/polished as described thereafter. They were embedded in oxidation by cold resin mixture (Escil Araldite CY230 and Hardener HY956), then ground with SiC-papers from 120 or 240-grit up to 1200-grit. After ultrasonic cleaning, final polishing was performed with textile enriched with 1µm hard particles until obtaining a mirror-like state.

Metallographic characterization

When they were still gold-covered only, the oxidized samples were observed using a Scanning Electron Microscope (SEM) – of the JEOL JSM 6010LA type – in Secondary Electrons (SE) mode. The scales were also characterized by Energy Dispersive Spectrometry (EDS) spot analysis. Prepared as cross-sections with mirror-like section state, the oxidized samples were observed with the SEM again, but in Back Scattered Electrons (BSE) mode. Local chemical compositions were determined by EDS spot analysis again (external and internal oxides).

RESULTS AND DISCUSSION

Global aspect of the oxidized samples

The macrographs issued from scanning with the office scanner and presented in Figure 1, illustrate the surface state of the nine oxidized samples (3 alloys × 3 temperatures). They allow seeing that, despite the rather low cooling rate (-5K min^{-1}), the external oxide scales suffered spallation. This was particularly severe for the Co-10Ni-30Cr alloy, nota-

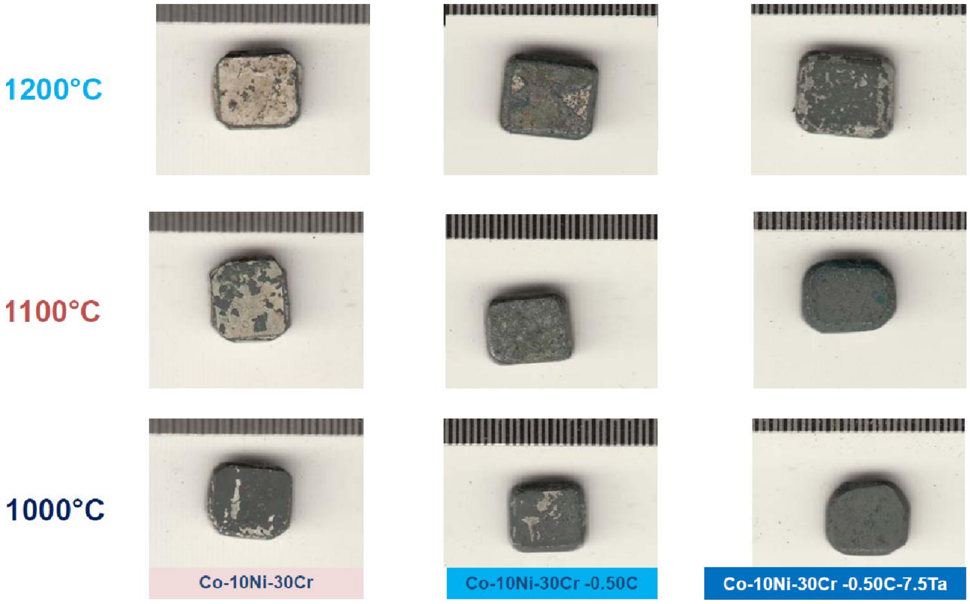


Figure 1 : Macrographs of the oxidized samples

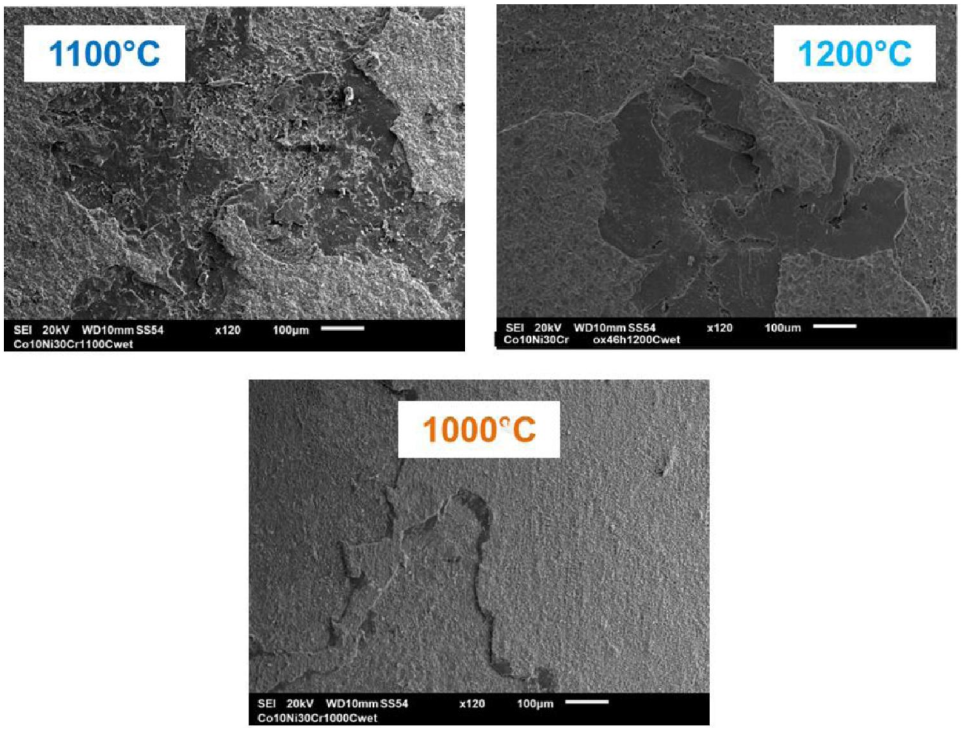


Figure 2 : SEM/SE micrographs of the Co-10Ni-30Cr alloy after 46 hours of oxidation at 1000 (bottom), 1100 (top left) and 1200°C (top right)

bly during cooling from 1200 and 1100°C. The Co-10Ni-30Cr-0.5C behaved better during the cooling from these two highest temperatures. The best one in this field is the third alloy, the Co-10Ni-30Cr-0.5C-7.5Ta one, notably for the cooling from the two lowest temperatures.

Scale characterization before cutting

The oxidized surfaces were observed with SEM in SE mode before electrolytic deposition of Ni. The micrographs presented in Figure 2 for the Co-10Ni-30Cr alloy, in Figure 3 for the Co-10Ni-30Cr-0.5C alloy and in Figure 4 for the Co-10Ni-30Cr-0.5C-7.5Ta alloy illustrated the oxide scales formed during the oxidation at the three temperatures.

SEM/EDS spot analysis performed on several

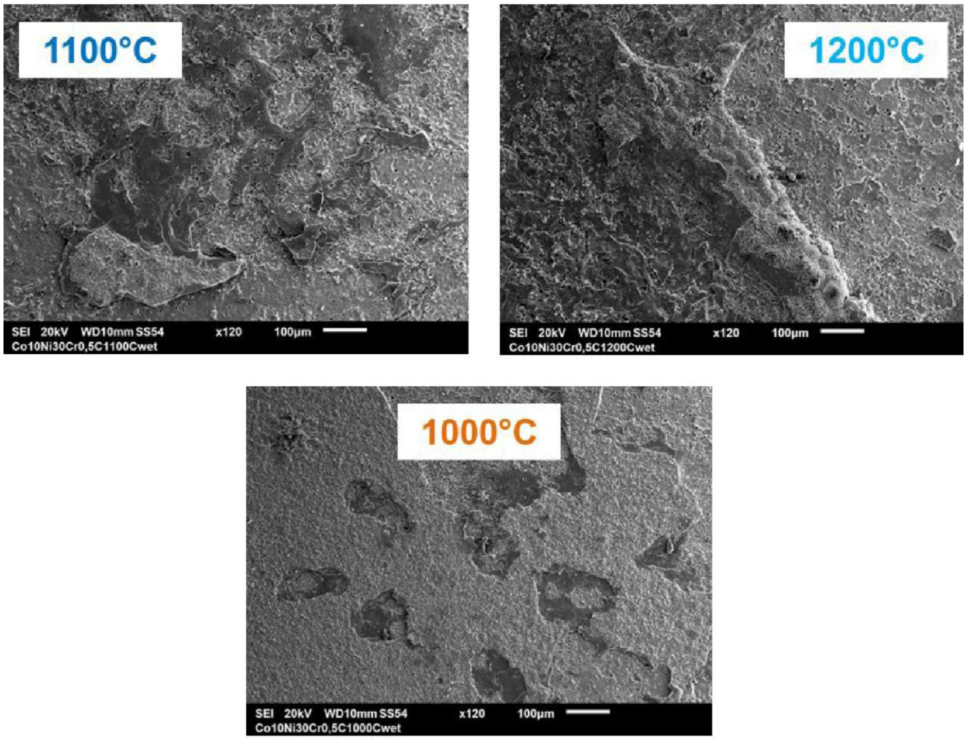


Figure 3 : SEM/SE micrographs of the Co-10Ni-30Cr-0.5C alloy after 46 hours of oxidation at 1000 (bottom), 1100 (top left) and 1200°C (top right)

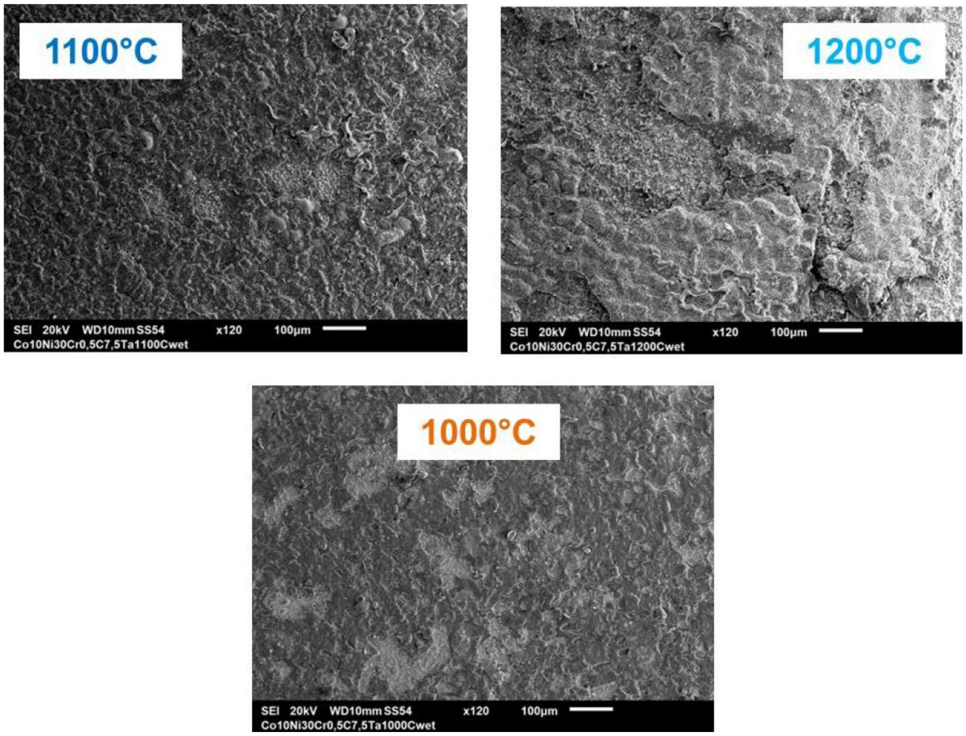


Figure 4 : SEM/SE micrographs of the Co-10Ni-30Cr-0.5C-7.5Ta alloy after 46 hours of oxidation at 1000 (bottom), 1100 (top left) and 1200°C (top right)

locations on the scales covering the Co-10Ni-30Cr alloy showed the presence of chromia, of (Co,Ni)O and of rare spinel $CoCr_2O_4$ oxide in the 1000°C-case, of Cr_2O_3, (Co,Ni)O and $CoCr_2O_4$ again in the 1100°C-case, and of Cr_2O_3 and (Co,Ni)O in the 1200°C-case. The EDS analysis performed on the denuded parts where appears the subjacent alloy revealed average chromium contents in extreme surface:

- of 16.32wt.%Cr (calculated from three values ranging from 16.01 to 16.79wt.%) in the 1000°C-case,
- of 17.69wt.%Cr (calculated from six values ranging from 16.56 to 19.62 wt.%) in the 1100°C-case,
- of 18.18wt.%Cr (calculated from seven values ranging from 16.44 to 20.89wt.%) in the 1200°C-case.

SEM/EDS spot analysis performed on several locations on the scales covering the Co-10Ni-30Cr-0.5C alloy showed the presence of chromia and (Co,Ni)O in the 1000°C-case, of Cr_2O_3 and (Co,Ni)O again in the 1100°C-case, and of Cr_2O_3, (Co,Ni)O and the spinel $CoCr_2O_4$ oxide in the 1200°C-case. On the denuded parts of alloy they also revealed the following average chromium contents in extreme surface:

- of 17.93wt.%Cr (calculated from three values ranging from 16.53 to 20.39 wt.%) in the 1000°C-case,
- of 18.11wt.%Cr (calculated from eleven values ranging from 15.23 to 19.92wt.%) in the 1100°C-case,
- of 19.84 wt.%Cr (calculated from eleven values ranging from 13.35 to 22.20 wt.%) in the 1200°C-case.

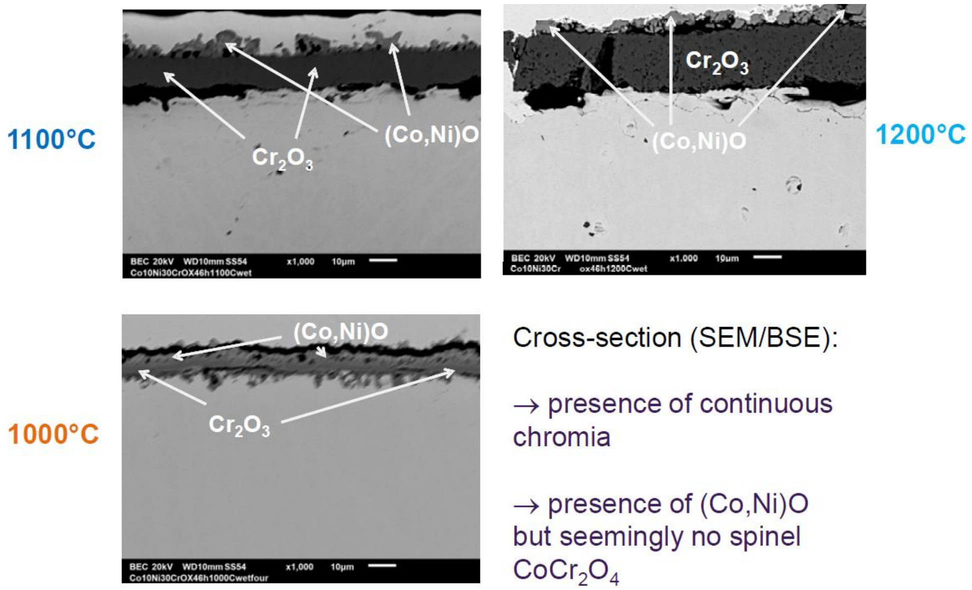
SEM/EDS spot analysis performed on several locations on the scales covering the Co-10Ni-30Cr-0.5C-7.5Ta alloy showed the presence of chromia, $CrTaO_4$ and also (Co,Ni)O in the 1000°C-case, of Cr_2O_3 and $CrTaO_4$ again but also of the $CoCr_2O_4$ spinel oxide in the 1100°C-case, and of Cr_2O_3 and $CrTaO_4$ oxide in the 1200°C-case. Because of very limited spallation during cooling the denuded parts of alloy were rare. Only a few values were determined by EDS:

- of 18.02wt.%Cr (the only value obtained) in the 1000°C-case,
- of 21.42 wt.%Cr (the only value obtained) in the 1100°C-case,
- of 23.31 wt.%Cr (calculated from three values ranging from 22.31 to 24.05 wt.%) in the 1200°C-case.

Tantalum was also detected but with very various contents in extreme surface.

Scale characterization after cutting

The oxidized samples were also observed in cross section. The surface and sub-surface states after oxidation at 1000, 1100 and 1200°C are illustrated by SEM/BSE micrographs in Figure 5 for the Co-10Ni-30Cr alloy, in Figure 6 for the Co-10Ni-30Cr-0.5C alloy and in Figure 7 for the Co-10Ni-30Cr-0.5C-7.5Talloy. The different oxides were

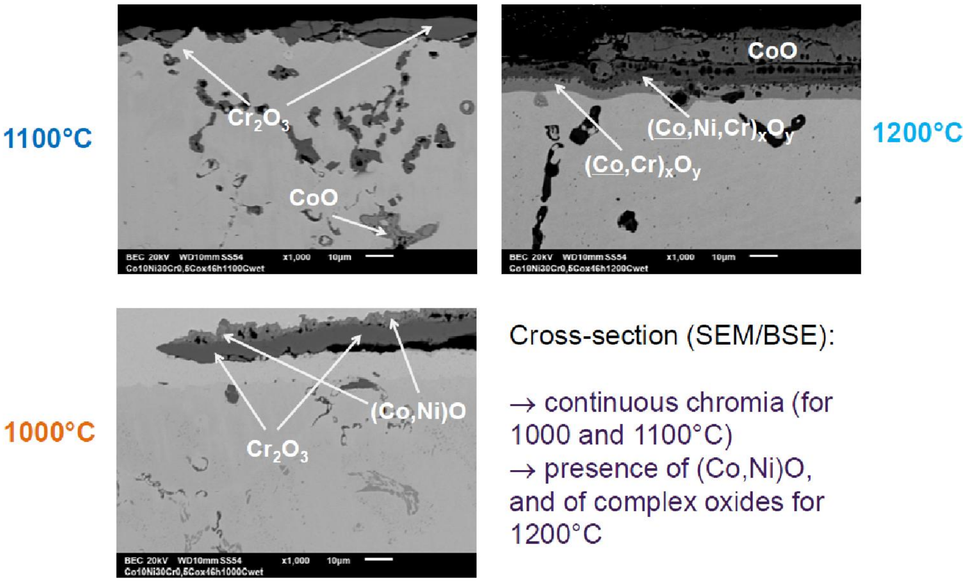


Cross-section (SEM/BSE):

→ presence of continuous chromia

→ presence of (Co,Ni)O but seemingly no spinel $CoCr_2O_4$

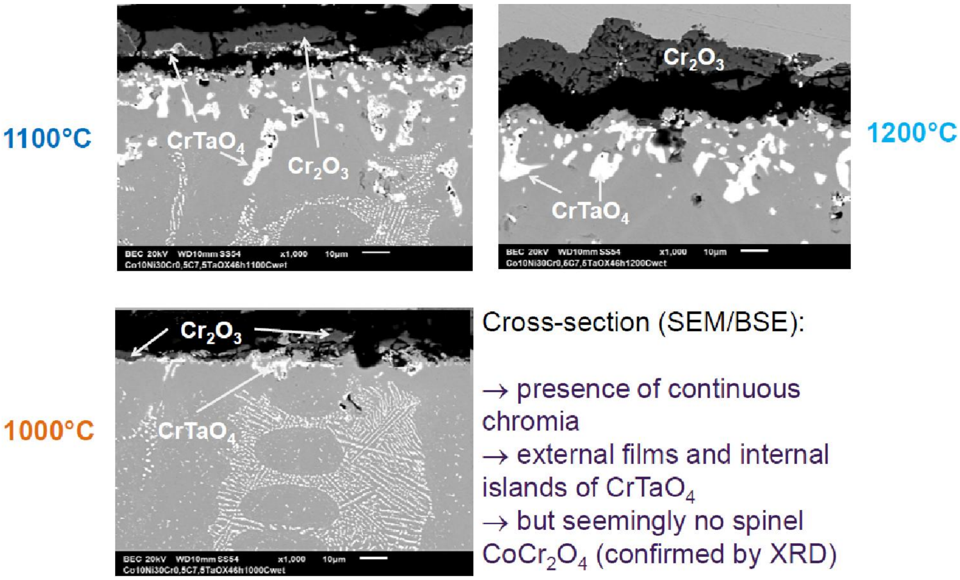
Figure 5 : SEM/BSE micrographs of the Co-10Ni-30Cr alloy after 46 hours of oxidation at 1000 (bottom), 1100 (top left) and 1200°C (top right)



Cross-section (SEM/BSE):

→ continuous chromia (for 1000 and 1100°C)
→ presence of (Co,Ni)O, and of complex oxides for 1200°C

Figure 6 : SEM/SE micrographs of the Co-10Ni-30Cr-0.5C alloy after 46 hours of oxidation at 1000 (bottom), 1100 (top left) and 1200°C (top right)



Cross-section (SEM/BSE):

→ presence of continuous chromia
→ external films and internal islands of $CrTaO_4$
→ but seemingly no spinel $CoCr_2O_4$ (confirmed by XRD)

Figure 7 : SEM/SE micrographs of the Co-10Ni-30Cr-0.5C-7.5Ta alloy after 46 hours of oxidation at 1000 (bottom), 1100 (top left) and 1200°C (top right)

identified in the parts of external scale remaining on the surface (generally confirming the results presented just before) while the internal oxidation state was specified: existence of internal oxides of different natures (Cr_2O_3, $CrTaO_4$), development of a carbide-free zone in the two last alloys, deeper in the alloy for a higher temperature.

General commentaries

In this wet atmosphere, the global behaviour of these alloys in oxidation at the considered high temperatures was not very different from their behaviours in dry air. However some little differences were nevertheless noticed. First it appeared that the alloys tended to more severely spall off during the cooling although these ones were realized in the same conditions (same parameters except the atmosphere of course). This was particularly true for the carbide-free ternary alloy whose external oxide scale was lost in major part. In contrast, the dependence of the oxide spallation at cooling was less clear for the two carbides-containing alloys. Concerning the external morphologies of the oxide scales as observed on surface before cutting with the SEM in SE mode, no systematic difference was evidenced between an alloy oxidized at a given temperature in dry air and the same alloy oxidized at the same temperature in wet air, neither in term of fineness nor in term of general morphology. When observed this time in cross section the oxide layer and the sub-surface were seemingly of the same natures and morphology for the first one, and of the same state of deterioration (surface roughness, internal oxidation, carbide-free depth) for the second one.

Differences only begin to appear with the results of the EDS measurements performed on surface on the denuded parts of the alloys. The chromium contents, which increase with the stage temperature for the two Co-10Ni-30Cr alloys oxidized in the two atmospheres, are systematically higher for the one oxidized in wet air than for the one oxidized in dry air (+5wt.%Cr more for 1000°C, +4wt.%Cr more for 1100°C and +3wt.%Cr more for 1200°C). This is the same type of difference for the Co-10Ni-30Cr-0.5C alloy (+2wt.%Cr more for 1000°C, +1wt.%Cr more for 1100°C for wet air than for dry air and almost the same Cr content for 1200°C) and for the Co-10Ni-30Cr-0.5C-7.5Ta alloy (+3wt.%Cr more for 1000°C and almost the same Cr content for 1200°C).

CONCLUSIONS

Thus, there were only a few differences of behaviour for these three alloys between wet air and dry air, about the oxide spallation at cooling for one of the three alloys, and concerning the chromium impoverishment on extreme surface. The two differences are however of importance since a degradation of the oxide scale adherence appears a deleterious effect of water vapour while, in contrast, higher Cr contents in extreme surface means that the loss of chromia-forming behaviour of the alloys maybe delayed to longer times. The post-mortem characterization ought to be carry on deeper, notably about the external oxide scale morphology, with finer observations. The rather small differences in behaviour for these 10%H_2O maybe means that greater differences may appear for air much richer in water vapour. This may be the subject of future work.

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