ISSN : 0974 - 7486 Volume 12 Issue 9

Trade Science Inc.

Materials Science

An Indian Journal

Full Paper

MSAIJ, 12(9), 2015 [342-349]

Influence of the water vapour content in air on the high temperature oxidation of cobalt-based alloys
part 1: results in dry air

Patrice Berthod[1,2,3]*, Lionel Aranda[3], Thierry Schweitzer[3], Albert Leroy[4], Alexandre Navet[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

Water vapour is often present in the hot oxidant atmospheres in which superalloys and other refractory alloys are used. If a lot of works have been carried out on steels and nickel-based alloys about the influence of water vapour on their high temperature oxidation, it seems that there are inversely no such studies concerning cobalt-based alloys. In this work three model alloys representing the bases of a great part of the existing cobalt-based superalloys were elaborated by foundry and tested in oxidation at high temperature in air enriched or not with water vapour. These tests were done in furnaces at 1000, 1100 and 1200°C for 46 hours, and the oxidation behaviours of these alloys were characterized by post-mortem examinations. In this first part, only the results obtained in dray air are presented. They showed that the Co-10Ni-30Cr alloy was not really chromia-forming, with the presence of cobalt oxide and spinel oxides beside chromia, and low chromium contents in extreme surface. The two other alloys, Co-10Ni-30Cr-0.5C and Co-10Ni-30Cr-0.5C-7.5Ta behave better, with more chromia and higher Cr contents in extreme surface. Differences were also seen about oxide scale spallation. These data will be compared to the ones which will be issued from the oxidation tests in humidified air, in the second part of this work.

KEYWORDS

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

INTRODUCTION

Besides deformation and creep under mechanical stresses or erosion phenomena, the use of metallic alloys in high temperature atmospheres generally induces also oxidation of their surfaces. Oxygen is often the main species responsible of this degradation[1,2] but other gaseous species such as water vapour[3], H_2[4], N_2[5], CO[6], CO_2[7], SO_2[8], HCl[9] and others may be present too and take part in the general surface degradation. Among these different corrosive gases water vapour is often encountered by turbine components and hot pieces working in industrial processes. Different refractory alloys are concerned by oxidation in presence of water vapour and steels or nickel-based alloys were extensively studied. Curiously, it seems that the cobalt-based alloys were almost never studied in high temperature oxidation. The purpose of this work is precisely to study the differences in their HT oxidation behaviour induced by the presence of water vapour.

The three model alloys studied in this work well represent most of the cobalt-based superalloys since they are a simplified version of them. They were oxidized in dry air for establishing a comparison base, and thereafter in air enriched with water. This first part of the study presents the preliminary results of oxidation in dry air. The results obtained in humidified air will be given in the second part.

EXPERIMENTAL

Choice of the alloys

Three alloys were elaborated by foundry practice. The first alloy is a ternary one Co(bal.)-10wt.%Ni-30wt.%Cr, wished rich in chromium to favour a good resistance against oxidation and corrosion at elevated temperature, and containing nickel in content high enough to stabilize the austenitic type of matrix (Face Centred Cubic) for avoiding crystallographic changes when temperature varies and to keep high strength at all temperatures[10-12] thanks to this compact atomic arrangement. The second one, Co(bal.)-10wt.%Ni-30wt.%Cr-0.5wt.%C, is similar to the previous one, except the additional presence of carbon which allows developing an interdendritic network of chromium carbides bringing improved mechanical strength at medium and high temperature. The third one, Co(bal.)-10wt.%Ni-30wt.%Cr-0.5wt.%C-7.5wt.%Ta, contains a fifth element, the strong carbide-forming behaviour of which allows replacing the previous carbides by tantalum carbides much more stable at very high temperature.

Elaboration of the alloys

The three alloys were fabricated using a High Frequency induction furnace (CELES). Parts of pure elements (Co, Ni, Cr, Ta: Alfa Aesar, > 99.9 wt.%; C: pure graphite) were placed in the water-cooled copper crucible of the furnace, were they were melted together and solidified as an alloy. The heating, {5 minutes-long}- isothermal stage in liquid state and the cooling were all realized in an inert atmosphere (300 mbar pure Ar) separated from outside with a silica tube. The weight of the obtained ingots was about 40 grams in each case.

Sample's preparation

Each compact-shaped ingot was sawed using a Buehler Abrasimet cutter to obtain a part for metallographic observation of the as-cast microstructures, and six parts for the oxidation tests (three in air and three in wet air[13]). The three samples for metallography characterization were embedded in a cold resin mixture (Escil Araldite CY230 and Hardener HY956). They were ground with SiC-papers from 120 or 240-grit up to 1200-grit, ultrasonically washed, the polished with textile rich in 1µm hard particles until obtaining a mirror-like state. The samples for oxidation tests, parallelepipeds whose dimensions were approximately 7 mm × 7 mm × 2 mm, were ground with 1200-grit SiC-paper with smoothing of their edges and corners.

Oxidation tests

The samples were exposed to a flow of dry synthetic air (80%N_2-20%O_2) in the hot zone of the furnace equipping a SETARAM SETSYS thermo-balance. 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

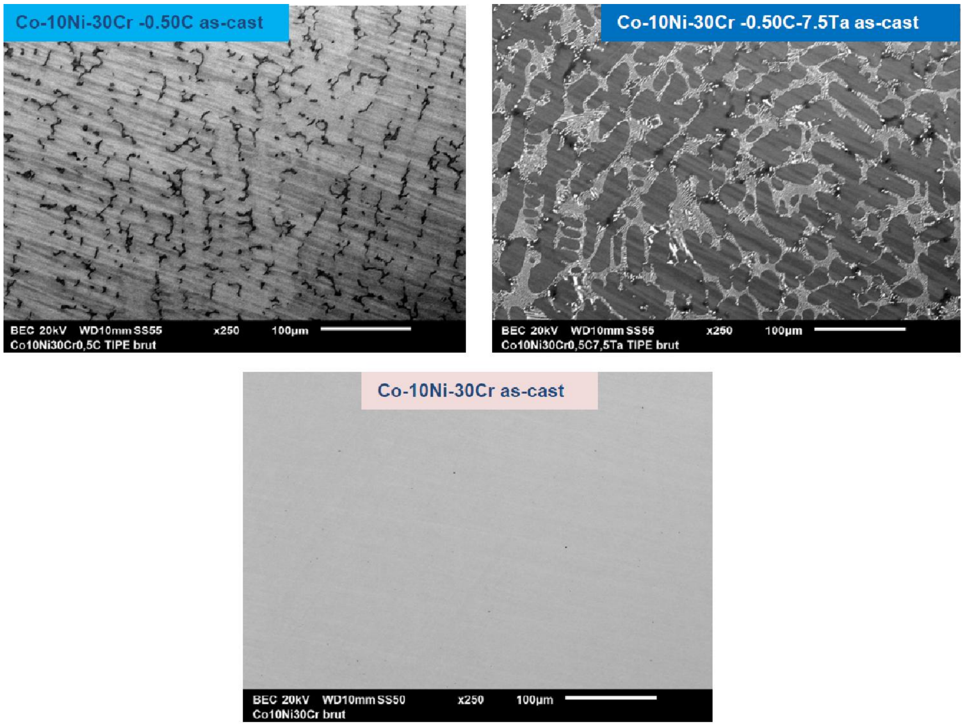


Figure 1 : The as-cast microstructures of the three alloys (SEM/BSE micrographs)

Ni layer allowed thereafter protecting the scales during the cutting in two parts which were embedded and ground/polished as described for the metallographic samples above.

Metallographic characterization

The gold-covered 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. The as-cast samples as well as the cross-sections prepared from the oxidized ones were observed with the SEM in Back Scattered Electrons (BSE) mode, and their local chemical composition by EDS spot analysis.

RESULTS AND DISCUSSION

Initial microstructures of the alloys

The microstructures of the three alloys in their as-cast states are illustrated by the three SEM/BSE micrographs presented in Figure 1.

The ternary alloy is seemingly single-phased while the two other alloys are constituted of a dendritic matrix of cobalt-based solid solution and of an inter-dendritic carbides network. In the quaternary alloy the carbides are chromium carbides, darker than matrix when observed with the SEM in BSE mode, while the carbides present in the quinary alloy are TaC carbides (white in BSE mode).

Global aspect of the oxidized samples

The macrographs issued from scanning with the office scanner and presented in Figure 2, 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. However, there is seemingly one alloy out of the three which was more resistant to this phenomena: the quinary TaC-containing alloy; this is particularly true for the cooling from 1000 and 1100°C. There was maybe also a tendency of more limited spallation in the case of the chromium-containing alloy, as seen after cooling from 1100°C only since the macrograph after cooling from 1000°C was not available for this alloy.

Scale characterization before cutting

The oxidized surfaces were observed with SEM

Figure 2 : Macrographs of the oxidized samples

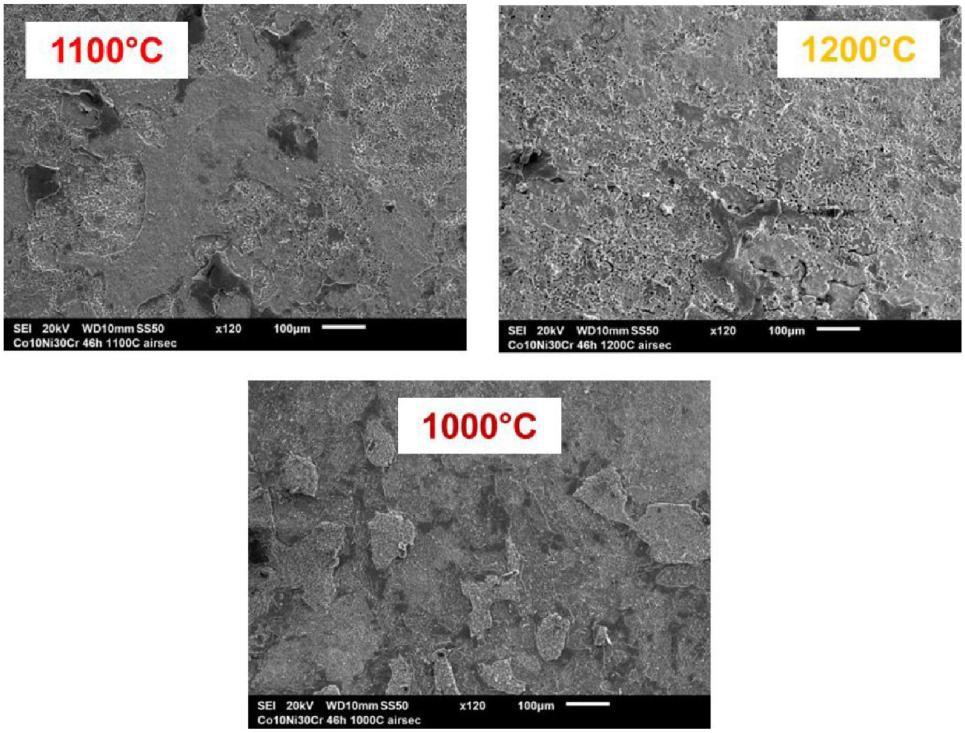


Figure 3 : SEM/SE micrographs of the Co-10Ni-30Cr alloy after 46 hours of oxidation at 1000 (bottom), 1100 (top left) and 1200°C (top right)

in SE mode before electrolytic deposition of Ni. The micrographs presented in Figure 3 for the Co-10Ni-30Cr alloy, in Figure 4 for the Co-10Ni-30Cr-0.5C alloy and in Figure 5 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 locations on the scales covering the Co-10Ni-30Cr alloy showed the presence of chromia and of the spinel $CoCr_2O_4$ oxide in the 1000°C-case, and of chromia and CoO in the 1100°C and 1200°C cases. The EDS analysis performed on the denuded parts where appears the subjacent alloy revealed average chromium contents in extreme surface:

- of 11.18 wt.%Cr (calculated from three values ranging from 9.46 to 13.49 wt.%) in the 1000°C-

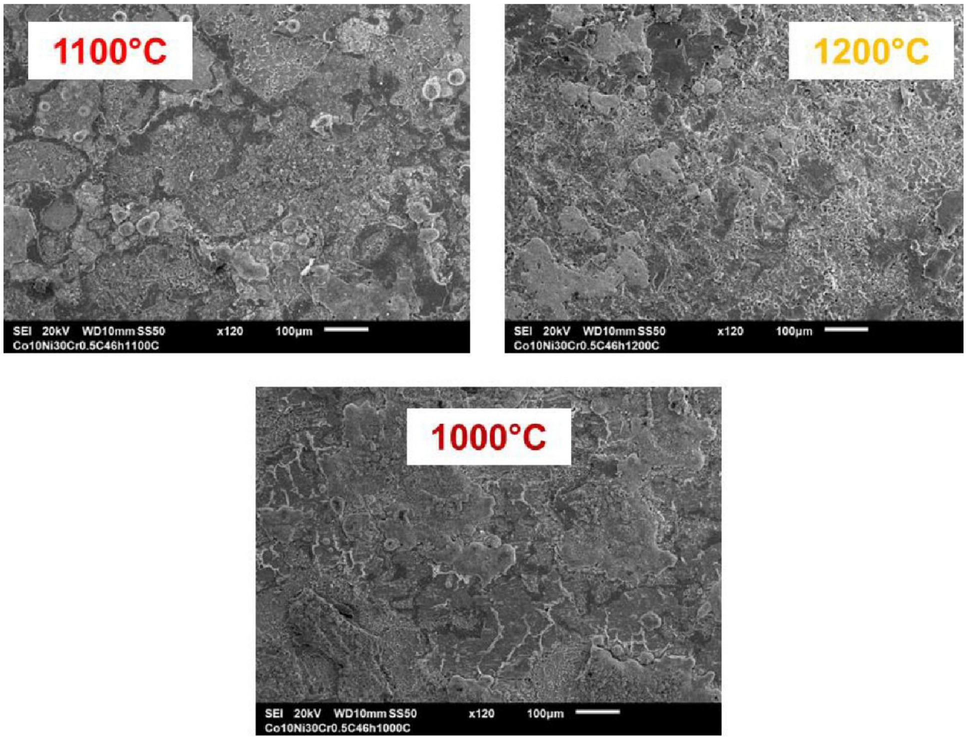


Figure 4 : SEM/SE micrographs of the Co-10Ni-30Cr-0.5C alloy after 46 hours of oxidation at 1000 (bottom), 1100 (top left) and 1200°C (top right)

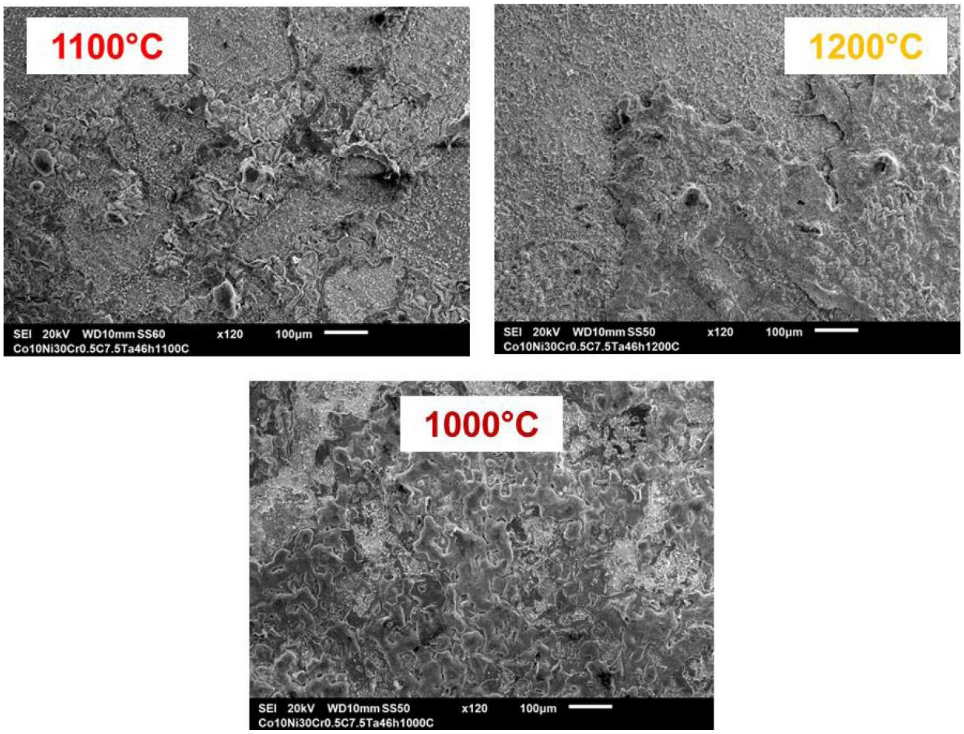


Figure 5 : SEM/SE micrographs of the Co-10Ni-30Cr-0.5C-7.5Ta alloy after 46 hours of oxidation at 1000 (bottom), 1100 (top left) and 1200°C (top right)

case,

- of 13.34 wt.%Cr (calculated from two values ranging from 13.02 to 13.65 wt.%) in the 1100°C-case,
- of 15.21 wt.%Cr (calculated from five values ranging from 12.58 to 16.40 wt.%) in the

1200°C-case.

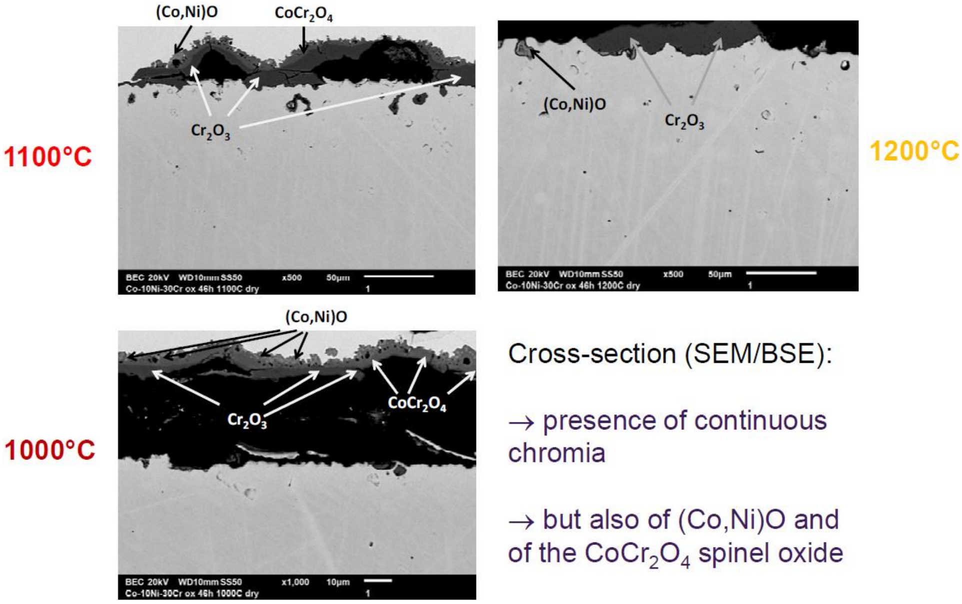
- For the Co-10Ni-30Cr-0.5C alloy, the EDS spot analyses showed the presence of chromia for the three temperatures. On the denuded parts of alloy they also revealed the following average chromium contents in extreme surface:
- of 18.04wt.%Cr (calculated from three values ranging from 16.86 to 19.01 wt.%) in the 1000°C-case,
- of 16.78 wt.%Cr (calculated from four values ranging from 14.94 to 19.21 wt.%) in the 1100°C-case,
- of 17.77 wt.%Cr (calculated from six values ranging from 16.98 to 18.60 wt.%) in the 1200°C-case.
- For the Co-10Ni-30Cr-0.5C-7.5Ta alloy, the EDS spot analyses showed the presence of chromia for the three temperatures, and probably of $CrTaO_4$ too. Since this third alloy did not really suffer oxide spallation the denuded parts of alloy were rather rare and it was not so easy to measure with EDS the average chromium contents in extreme surface; however some results were obtained for 1000°C and for 1200°C:
- of 21.29 wt.%Cr (only one value) in the 1000°C-case,
- of 22.91 wt.%Cr (calculated from two values ranging from 21.29 to 24.53 wt.%) in the 1200°C-case.

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 6 for the Co-10Ni-30Cr alloy, in Figure 7 for the Co-10Ni-30Cr-0.5C alloy and in Figure 8 for the Co-10Ni-30Cr-0.5C-7.5Ta alloy. The different oxides were 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

When oxidized at high temperature the three alloys, despite their rather high contents in chromium, the three alloys are not really chronia-forming. Indeed, CoO or the $CoCr_2O_4$ spinel oxide are present together with chromia. This is particularly the case of the two Ta-free alloys. The Co-10Ni-30Cr-0.5C-7.5Ta alloy seems having behaved more as a chromia-forming alloy but the discrete presence of spinel oxide was sometimes detected. In addition significant quantity of the complex $CrTaO_4$ has ap-

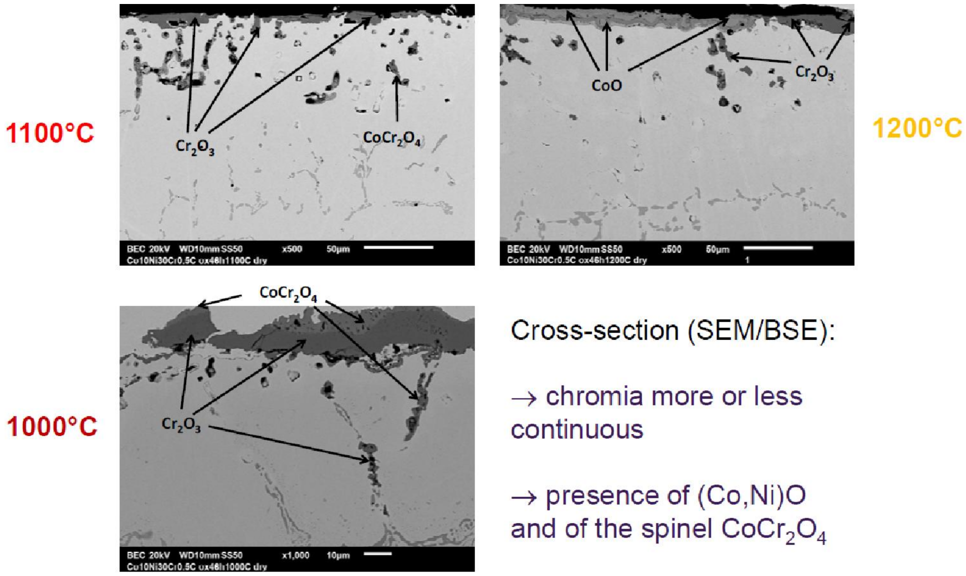


Cross-section (SEM/BSE):

→ presence of continuous chromia

→ but also of (Co,Ni)O and of the $CoCr_2O_4$ spinel oxide

Figure 6 : 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)

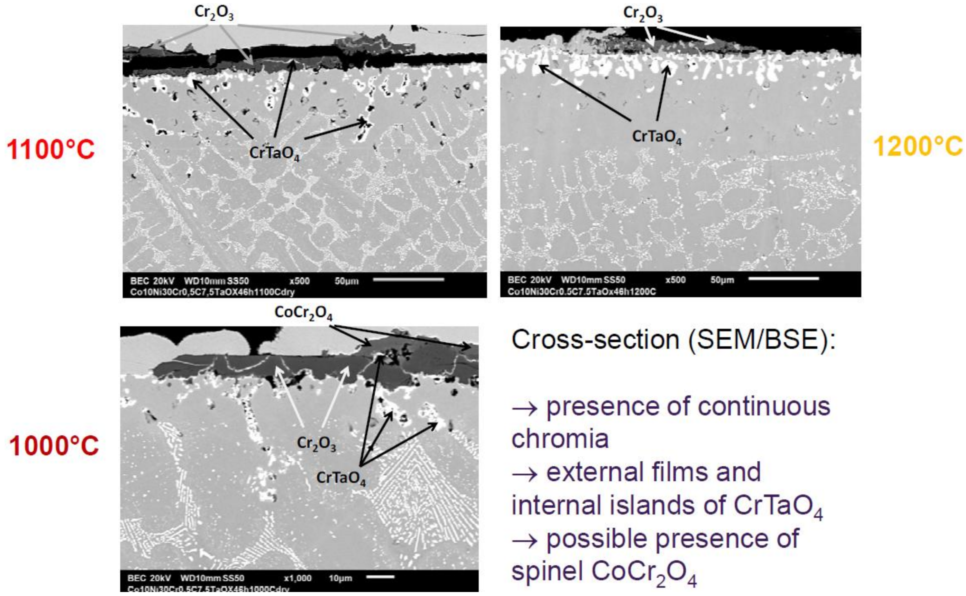


Cross-section (SEM/BSE):

→ chromia more or less continuous

→ presence of (Co,Ni)O and of the spinel CoCr$_2$O$_4$

Figure 7 : 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$_4$
→ possible presence of spinel CoCr$_2$O$_4$

Figure 8 : 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)

peared, by internal oxidation but also as films immersed in the external chromia scale. Because of spallation (more limited than for the two Ta-free alloys), this complex oxide of both Cr and Ta has appeared on surface here and there. Differences between the alloys was also noticed concerning the chromium contents in extreme surface: lower for the Co-10Ni-30Cr alloy (about 13 wt.%Cr), than for the Co-10Ni-30Cr-0.5C one (around 17 wt.%), and lower for both of them than for the Co-10Ni-30Cr-0.5C-7.5Ta alloy (about 22 wt.%Cr). These differences have to be associated to the behaviour chromia-forming or not of these alloys, and they probably result from the more or less easy diffusion of chromium outwards. When present, inter-dendritic carbides generally help this diffusion and allows better Cr supplying of the oxidation front.

CONCLUSIONS

With these first oxidation tests carried out in dry air, one constituted an important quantity of data characterizing the oxidation behaviour of these three cobalt-based alloys. They will be compared to the similar ones which will be obtained in humidified air for the same alloys and the same thermal cycles[13]. If they exist he effects of the presence of water vapour on the behaviour of cobalt-based alloys in oxidation at high temperature will be highlighted, interpreted and explained.

REFERENCES

[1] P.Kofstad; ‘High temperature corrosion’, Elsevier applied science, London, **(1988)**.

[2] D.Young; High Temperature oxidation and corrosion of metals, Elsevier, Amsterdam, **(2008)**.

[3] A.Galerie, M.R.Ardigo, P.Berthod, W.Chandra-Ambhorn, S.Chevalier, P.Y.Hou, F.Rouillard; Chapter 1 : Influence of water vapor on high-temperature oxidation of chromia-forming materials, in: French activity on high temperature corrosion in water vapor, (Eds). Chevalier and J.Favergeon, Trans Tech Publications Ltd, Durnten-Zurich, Switzerland, **(2014)**.

[4] S.W.Kim, H.G.Lee; Steel Research International, **80(2)**, 121 **(2009)**.

[5] Z.Zurek, A.Jaron, A.Stawiarski, A.Gil; Materials Science Forum, **566**, 654-656, **(2010)**.

[6] F.Rouillard, C.Cabet, K.Wolski, M.Pijolat; Corrosion Science, **51(4)**, 752 **(2009)**.

[7] P.Promdirek, G.Lothongkum, S.Chandra-Ambhorn, Y.Wouters, A.Galerie; Oxidation of Metals, **81(3-4)**, 315 **(2014)**.

[8] Z.Zurek, A.Stawiarski, A.Jaron; Ochrona przed Korozja, **54(6)**, 328 **(2011)**.

[9] Y.Sato; Yosha, **37(1)**, 20 **(2000)**.

[10] E.F.Bradley; ‘Superalloys: A technical guide’, ASM International, Metals Park **(1988)**.

[11] M.J.Donachie, S.J.Donachie; ‘Superalloys: A technical guide” (2nd edition), ASM International, Materials Park, **(2002)**.

[12] C.T.Sims, W.C.Hagel; “The superalloys”, John Wiley & Sons, New York **(1972)**.

[13] L.Aranda, P.Berthod, T.Schweitzer, A.Navet, A.Leroy; Materials Science: An Indian Journal, to be submitted.