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Behavior of Two Foundry Cobalt-Based Alloys Exposed to a Hot Complex Gaseous Mixture Simulating the Atmosphere in a Waste-to-Energy Boiler. Part 1: Case of the Alloy Exposed to the Complex Gas Stream

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Abstract: The refractory materials required for waste-to-energy boilers endure severe working conditions, such as exposure to heat and hot oxidation / corrosion. Thanks to their high temperature properties cobalt-based alloys may respond to these properties requirements. In this work two model alloys based on cobalt and rich in chromium were elaborated by casting and samples were prepared by cutting and polishing. These samples were exposed, one to a hot complex gaseous mixture particularly aggressive reproducing the atmosphere in WtE boilers in service (presence of water vapor, di-oxygen, carbon di-oxide, hydrogen chloride), and the other to synthetic ashes, both for more than two hundreds hours. After test the samples were characterized by X-ray diffraction and SEM observations. On sample exposed to the complex gas stream a {10 to 15 μ m}-thick oxide scale formed on the surface of the sample exposed to the gas mixture. It involved all the elements of the alloy and it obviously developed both inwards and outwards as suggested by the position of the oxidized carbides.

Keywords: Cobalt-chromium alloys, HCl gas, CO₂, Water vapour, Hot corrosion.

INTRODUCTION

The waste-to-energy boilers are, in service, exposed to fireside corrosion [1]. These metallic parts stay in a very aggressive environment where gases such as SO₂, SO₃ and HCl are present [2], as well as the ashes formed [3, 4]. Corrosion-resistant materials or coatings to protect them must be used to allow lifetimes great enough [5]. For instance refractory alloys based on iron and nickel and rich enough in chromium [6] may be suitable for this application while coatings may be envisaged for a better behaviour [7]. Refractoriness high enough and resistance against hot corrosion may be also brought by cobalt-based superalloys. Indeed most of them present high melting points [8] and contain 25 to more than 30 wt.% of chromium [9]. This allow them to be used for long lifetimes in severe conditions mixing mechanical solicitations, hot corrosion by melts and hot oxidation by air or burner gases [10].

The subject of the present study is to test two model alloys belonging to this category, a one strengthened by chromium carbides and another one reinforced by

tantalum carbides, in an experimental apparatus reproducing the working conditions of WtE boilers. This aims to estimate the potential interest of chromia-forming cobalt-based superalloys for this type of application for which iron-based or nickel-based alloys are generally employed. In this first part this is the case of the sample exposed to the complex gas stream which will be studied.

MATERIALS AND METHODS

Origin of the Alloy Used in This Study

A sample coming from ingots especially elaborated by foundry in the frame of an earlier study, which was still available, was used for this work. This alloy, called "TAC", is rather complex. Its chemical composition contains cobalt as base element (bal.), 10 wt.%Ni for stabilizing the austenitic structure of the matrix, 30 wt.%Cr for favouring a chromia-forming behaviour to correctly resist both oxidation and corrosion, 0.5wt.%C for promoting the formation of interdendritic carbides, and 7.5wt.% of tantalum for obtaining TaC carbides as single carbides present. This composition, successfully obtained in the alloy, led to the wished microstructure: dendritic matrix of a solid solution of cobalt with nickel and chromium atoms in substitution and carbon in insertion, and eutectic script-like tantalum carbides in the interdendritic spaces.

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The Experimental Apparatus Used

The apparatus with which the tests were carried out is presented in Figure 1. The conditions of a WtE boiler in service were reproduced, thanks to a gas burner allowing the generation of a hot mixture gas of interest (H_2O , CO_2) with introduction of industrial scoria in the produced combustion gases. The ashes were introduced by a screw feeder. Pure SO_2 came from a bottle in which it was present as a compressed gas and HCl was introduced as an aqueous solution which was injected using a metering pump. The generated smokes were washed by a water shower. Scoria was recovered using a decanter. The "TAC" sample, which was suspended, was exposed to the gas mixture (1100 ppm of HCl , 18%.vol H_2O , 8%.vol O_2 and 5%.vol CO_2). It was exposed at $550 \pm 10^\circ\text{C}$ during 260 hours in these conditions.

Characterization of the Samples After Tests

Prior to metallographic preparation the tested

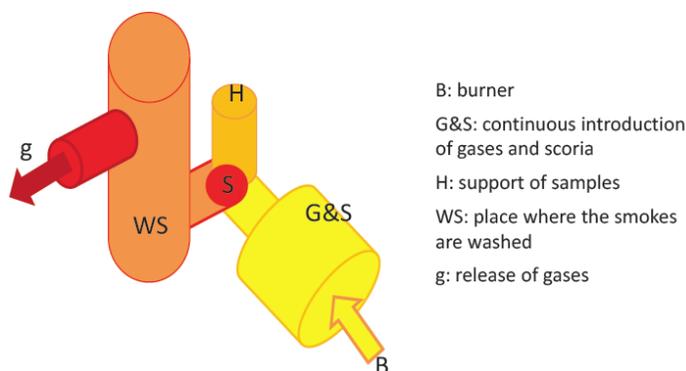


Figure 1: Scheme of the apparatus used for reproducing the conditions known by WtE boilers in service.

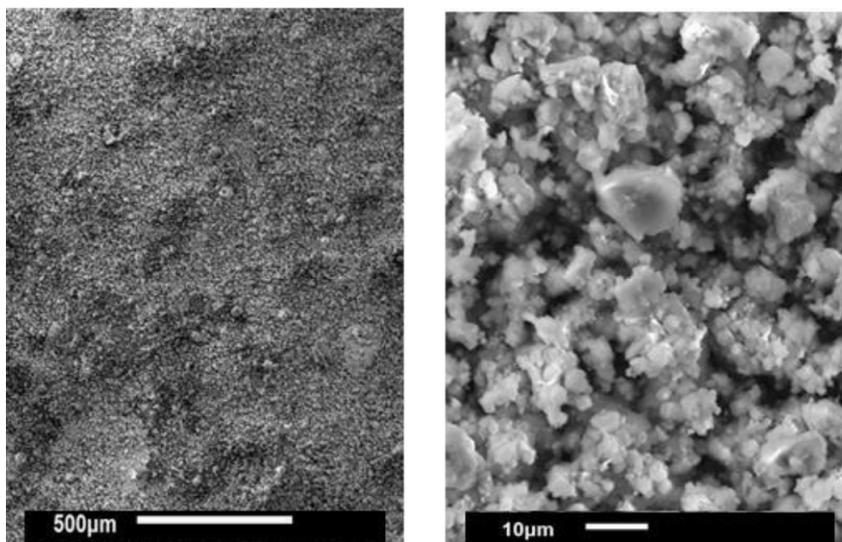


Figure 2: Surface observations at low (left) and high (right) magnification (SEM, SE mode).

sample was subjected to X-ray diffraction (XRD). It was thereafter embedded in a cold resin mixture and cut. It was then ground using SiC papers with grades varying from 240 to 2400. Water was avoided as lubricant to do not damage the corrosion products. Kerdane (dearomatized petrol, cleaning and degreasing) was used instead. Textile disk enriched with $1\mu\text{m}$ diamond particles were used for the following polishing step (lubricant: absolute ethanol). Examinations were carried out using a JEOL JSM6010LA Scanning Electrons Microscope (SEM) and to Energy Dispersive Spectrometry (EDS) measurements. Two modes were used: Secondary Electrons (SE) and Back Scattered Electrons (BSE).

RESULTS

Some SEM micrographs of the surface of the "TAC" sample are given in Figure 2. They are taken in the SE imaging mode, at two different magnifications. The observed corrosion products are composed of oxides

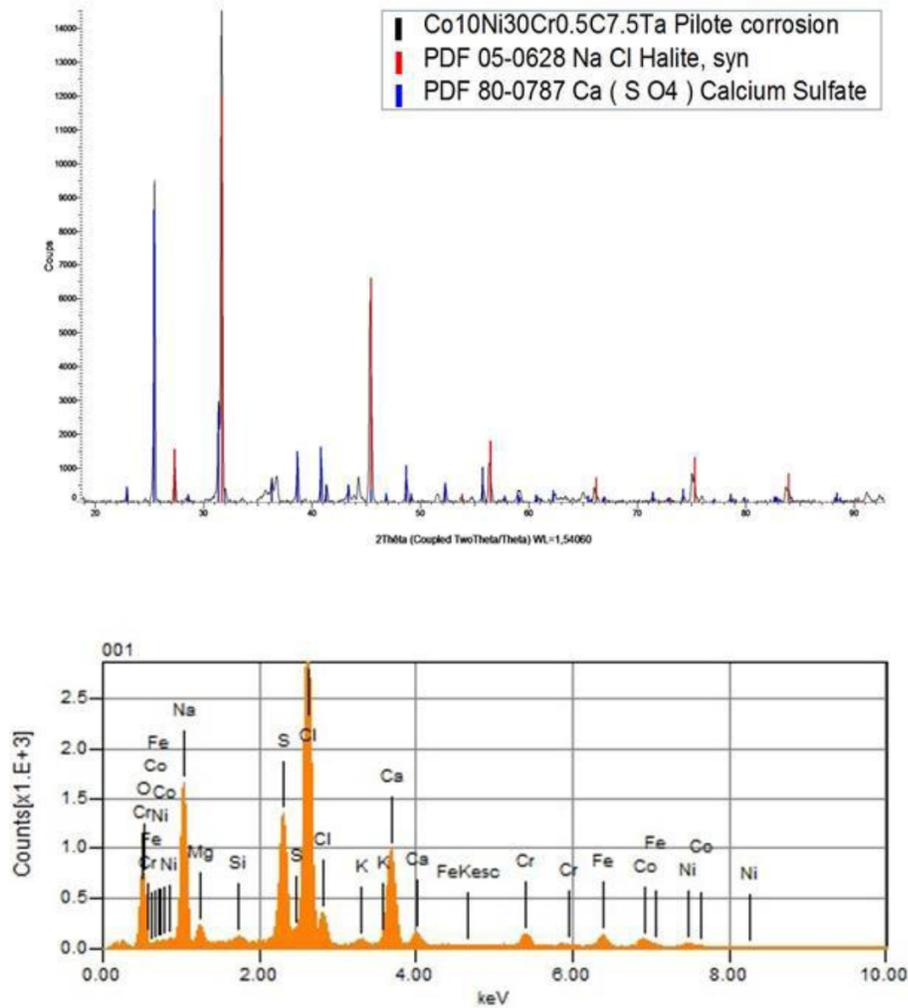


Figure 3: X-ray diffractogram (top) and EDS spectrum (bottom) acquired on the corrosion products formed over the “TAC” sample after test.

and crystals coming from the scoria introduced upstream: NaCl and $\text{Ca}(\text{SO}_4)$ as identified by XRD and EDS (Figure 3).

SEM micrographs taken in BSE mode on the tested sample after its cross-sectional metallographic preparation, with again two magnifications, are displayed in Figure 4. The corrosion products as well as the subsurface degradation of the alloys can be observed. EDS spot analyses, carried out here and there in the layer of corrosion products, evidence the presence of a (Co, Ni)O oxide and of the CoCr_2O_4 spinel oxide, as well as inclusions, some of them made of $\text{Ca}(\text{SO}_4)$ (Figure 5).

The eutectic TaC carbides, present in the interdendritic spaces, seem to be unchanged, close to the oxidation front (no inwards development of a carbide-free zone) as well as in the bulk (they kept their script morphology, and did not become fragmented).

However, at high magnification, it appears that oxidation developed inwards. This consumed the alloy matrix and transformed the tantalum carbides in oxides having the same morphology as the initial carbides.

DISCUSSION

Despite the rather low temperature in this experiment the tested alloy was severely degraded by regards to how it is to behave when exposed to air at much higher temperatures, this demonstrating the aggressiveness of the WtE environment.

Concerning this “TAC” alloy the average thickness of the oxide scales formed is of the same order of magnitude as when this alloy is exposed at 1000°C during about fifty hours, as observed in an earlier study [11]. In contrast with oxidation at 1000°C in air the oxidation products are here very different. The external oxide scales obtained at 1000°C after 50 hours of

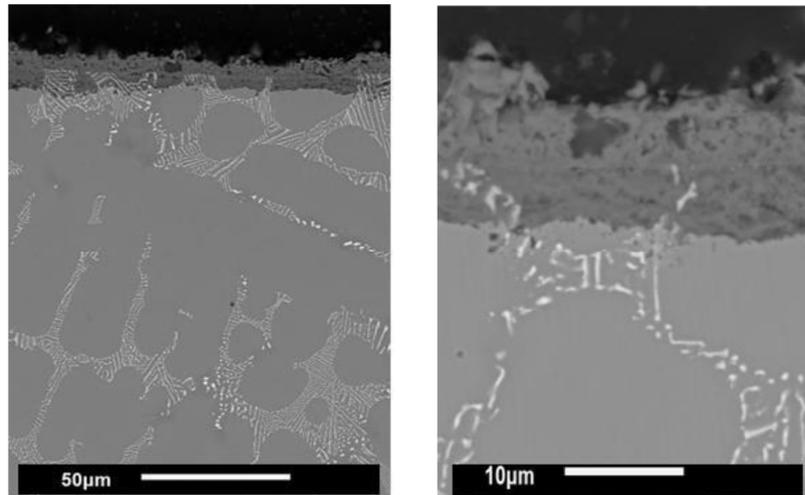


Figure 4: Surface observations at low (left) and high (right) magnification (SEM, SE mode).

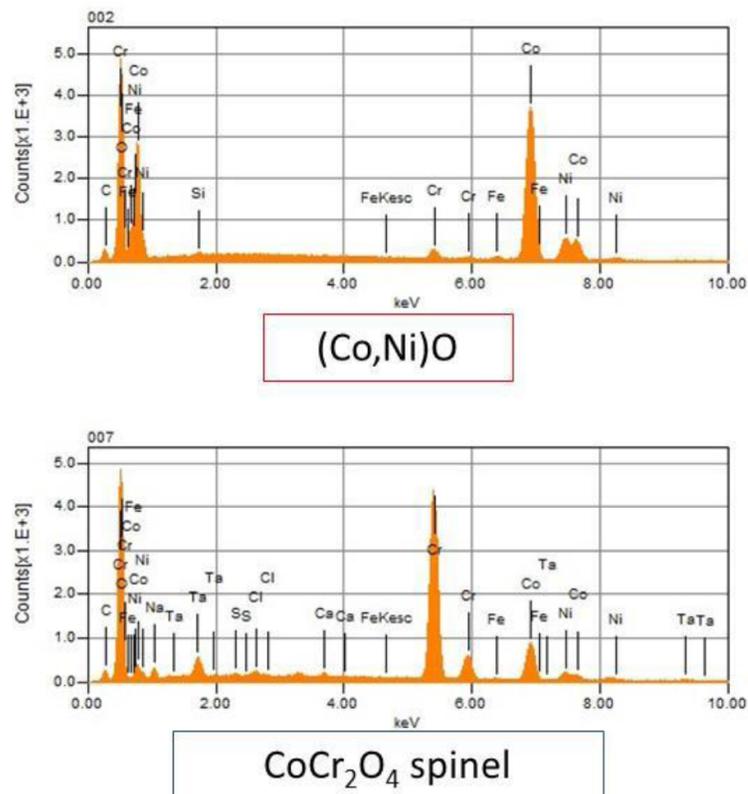


Figure 5: Identification of oxides present on surface and in subsurface of the "TAC" sample.

exposure to air was a continuous compact chromia scale developed outwards (Figure 6). In this chromia scale CrTaO₄ was present here and there as films mixed with the chromia scale. This oxide was also present in the outer part of the subsurface. After oxidation at 1000°C again, a zone losing its TaC carbides initially present developed inwards from the alloy/external oxide scale interface. In the present case the external oxide is porous and must be considered as

composed of two distinct layers. The outer one did not contain other oxides than (Co, Ni)O and CoCr₂O₄ spinel while the inner layer also contains CrTaO₄ oxides. Considering the distribution and morphology of these CrTaO₄ oxides, these ones appear as resulting of the *in situ* oxidation of the TaC carbides initially present in the same location (interdendritic) with the same morphology (script-like).

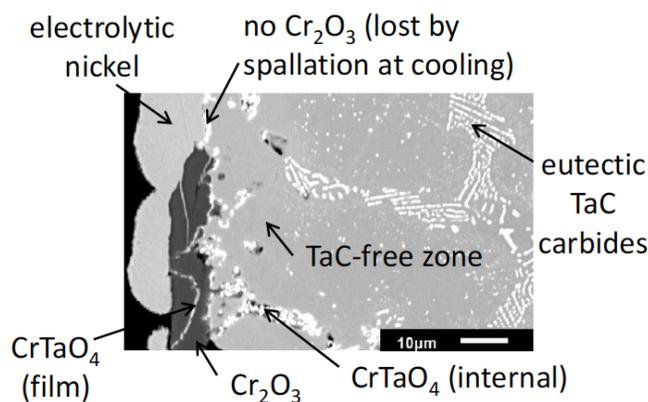


Figure 6: SEM/BSE micrograph of oxidized surface and subsurface of the “TAC” alloy oxidized at 1000°C after 46h of exposure to synthetic air.

Probably due to the low temperature of the test, one can guess that the big Ta atoms were not able to diffuse toward the oxidation front as they do at 1000°C in such alloy (i. e. with formation of films of CrTaO_4 or subsurface accumulation of CrTaO_4) and they were oxidized where they were, by oxygen diffusing inwards. The part of oxide spinel oxide and cobalt oxide formed in the vicinity of these script-like tantalum oxide probably grew inwards by anionic diffusion while the outer part grew outward by cationic diffusion. In this hypothesis, by its in situ oxidation tantalum played the role of marker of the initial surface.

CONCLUSIONS

Despite it earlier proved its high chemical resistance in air at much higher temperature than in the present study this cobalt alloy was severely corroded in the complex atmosphere generated here to simulate the working conditions of WtE boilers. Only beginnings of possible explanations were formulated to interpret the different types of degradation affecting this alloy and thorough investigations stay to be carried out to understand much better what occurred to this alloy. But this one clearly appears to be able to correctly behave in such situation in its present state. Indeed this TaC-containing alloy suffered fast degradation with both outward and inward growth of the external scales,

these ones being furthermore clearly not protecting taking into account their natures (oxide of cobalt and spinel, no chromia) and their porosities states. In the second part of this work, this will be the case of the second cobalt alloy which will be examined [12], by characterization of its degradation in another context, exposed to the same complex gas stream and to model ashes in which it was immersed.

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