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Degradation at 550°C of cast chromium-rich cobalt-based alloys exposed to a H₂O-O₂-CO₂-HCl gaseous mixture

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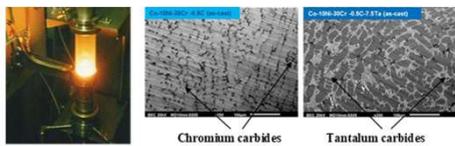
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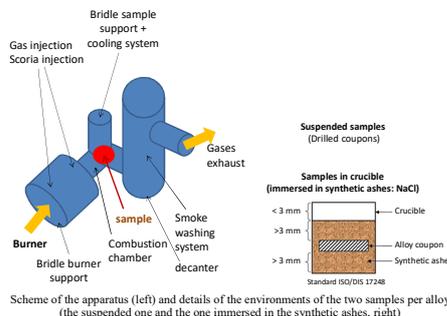
For applications at moderate temperature, even in presence of intense mechanical stresses and very aggressive fluids, alloys which are needed can be ones which may be different from the superalloys used as turbine blades in aeronautics or power generation, and cheaper than them. This is for example the case of high performance stainless steels, nickel alloys, or why not cobalt-based alloys. These alloys may bring interesting mechanical strength and correct resistance against oxidation by gases and corrosion by molten substances. Cobalt alloys have rather found new applications such as hot tools for working molten glass. The oxidative gaseous milieu in which cast cobalt-based superalloys work the most often are dry or wet air, or mixtures of burner gases. However there are applications, notably in the waste-to-energy (WtE) plants, in which hot gases are present as mixtures of many very aggressive chemical substances (in WtE boilers), for which cobalt-based superalloys may be considered. Their behaviour in so highly hostile environment seems to have been never investigated. This is why one decided here to test some cast cobalt-based alloys in hot environments typical of waste valorisation for energy production.

Work carried out in the frame of the research activities of the GDR N°3583 "EVACOHT" (Groupe De Recherche "Effet de la Vapeur d'eau en Atmosphères complexes sur la Corrosion et l'Oxydation à Haute Température" of the CNRS (Centre National de la Recherche Scientifique))

Experimental



On-going elaboration of an alloy by HF induction melting (left) and SEM[®]/BSE^{**} micrographs of the microstructures obtained for the two alloys (right)
[®] Scanning Electronic Microscopy; ^{**} Back Scattered Electronic mode



Sample which was suspended
 Sample which was immersed
 Macrophotos of the two types of samples being metallographically prepared

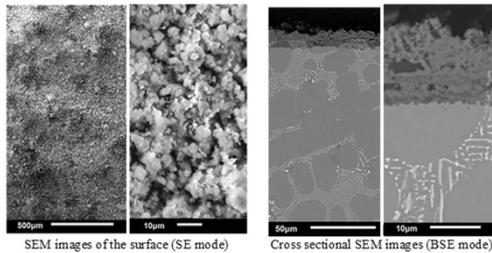
Corroded samples embedded in cold resin and polished in special conditions (ground under Kerdane, finished under ethanol)

SEM/SE&BSE surface and cross-sectional examinations, XRD runs

Two cobalt-based alloys cast by high frequency induction melting
 Co(bal.)-10Ni-30Cr-0.5C (-7.5Ta)

Exposed at 550°C for 260h to conditions reproducing the working conditions of a WtE boiler (either to gas mixture: several hundreds ppm HCl, several tens % vol H₂O, about ten % vol O₂ and CO₂) or to synthetic ashes (NaCl)

Results



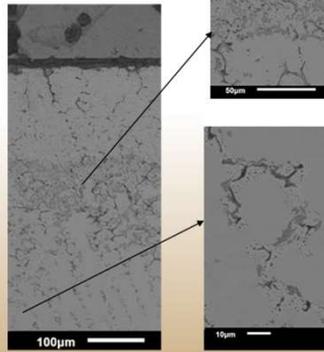
Surface SEM/SE observations (left) and cross-section SEM/BSE observation of the suspended Co-10Ni-30Cr-0.5C-7.5Ta alloy

Suspended alloys: example of the Co-10Ni-30Cr-0.5C-7.5Ta one (SEM/SE and BSE, EDS, XRD):

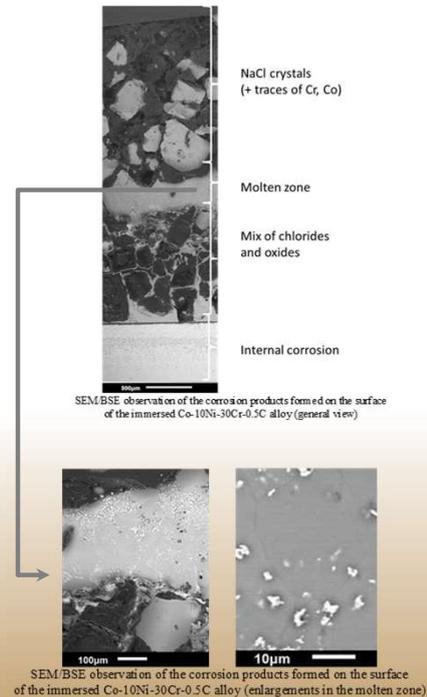
- presence of (Co,Ni)O and CoCr₂O₄ (spinel) oxides
- presence of also CaSO₄ in the oxide scale
- no obvious changes for the alloy when observed at low magnification (no carbide-free zone, TaC carbides still scriptlike-shaped)
- at high magnification: inward development of oxidation, consumption of matrix, *in situ* conversion of the TaC carbides into tantalum oxides with conservation of their morphology

Immersed alloys: example of the Co-10Ni-30Cr-0.5C one (SEM/BSE and EDS, XRD):

- severely corroded, absence of any protecting oxide, internalk oxidation over more than 500µm in depth
- different layers of corrosion products
- presence of an intermediate melting zone containing mainly NaCl with traces of Co and Cr
- presence of CoCl₂ and (perhaps) of CoCl₃ crystals, suggesting the formation of chlorides eutectic with low melting point



Internal corrosion of the Co-10Ni-30Cr-0.5C alloy (oxidation / chloridation of the network of chromium carbides over a depth of more than 500 µm)



SEM/BSE observation of the corrosion products formed on the surface of the immersed Co-10Ni-30Cr-0.5C alloy (enlargements in the molten zone)

Conclusion

Usually devoted to uses at temperatures much higher than the one applied in this work, the two considered cobalt-based alloys paradoxically suffered here much more than when they are exposed to air or in contact with molten glasses for example at temperatures higher than 1000°C. It is true that the 550°C that they knew here were much lower than what is required to allow a significant development of a carbide-free zone or fragmentation and coarsening of the interdendritic carbides, chromium carbides or TaC. But in the present context the burner gases and the synthetic ashes acted as redoubtable corrosive fluids against which chromia did not succeeded in forming to obstruct the induced deteriorating phenomena. After these factual descriptions of the degradations, next work will aim to understand what happened for the suspended sample as well as for the immersed ones. Some starts of explanations, extrapolated from the active oxidation in the case of steels, were suggested in this work but now they need to be deepened and completed.