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# High Temperature Oxidation Behavior of Cast Cobalt-Based Superalloys versus the Nature of their Reinforcing Carbides

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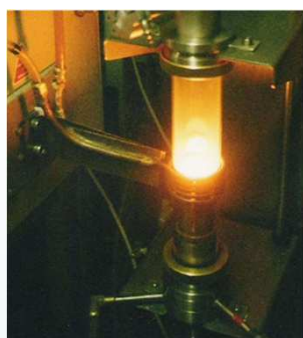
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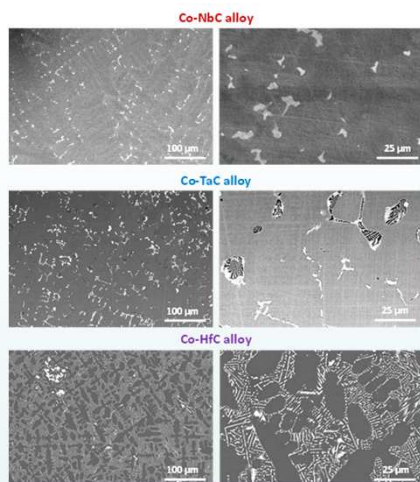
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In some cases the compulsory resistance against high temperature corrosion by molten substances leads to choose chromia-forming alloys instead  $\gamma/\gamma'$  nickel-based superalloys [1, 2]. Cast cobalt-based superalloys represent then an interesting alternative solution since they may benefit from hot oxidation and corrosion resistance as well as high mechanical resistance at elevated temperature. Some of them are even able to be used at temperatures as high as 1200°C, thanks to their interdendritic network of very refractory MC-type carbides. Indeed the presence of this type of mechanical reinforcement does not limit the content in chromium and, on the other hand, the script-like morphology of many of these MC carbides [3] is particularly efficient for combatting creep. This is the case of the NbC, TaC and HfC [4], provided that these carbides are present in quantity high enough to really bring significant strength. For that carbon contents as high as 0.5 wt.% and M present with the same atomic content as carbon are required. But one can fear that the rather high resulting mass contents (from 3.9 wt.% for niobium to 7.5 wt.% for Ta, for instance) may significantly change the initial high temperature oxidation behavior of the alloy's base. In this work three (Co-25wt.%Cr-0.5wt.%C)-based alloys containing 3.9 wt.% Nb, 7.5 wt.% Ta or 7.4 wt.% Hf, contents respecting the atomic equivalence between C and the M element, condition for promoting the formation of MC carbides exclusively. These alloys were elaborated by high frequency induction melting under inert atmospheres and submitted to thermogravimetry oxidation tests at 1200°C to specify their mass gain kinetics at this level of temperature of use to which they are devoted.

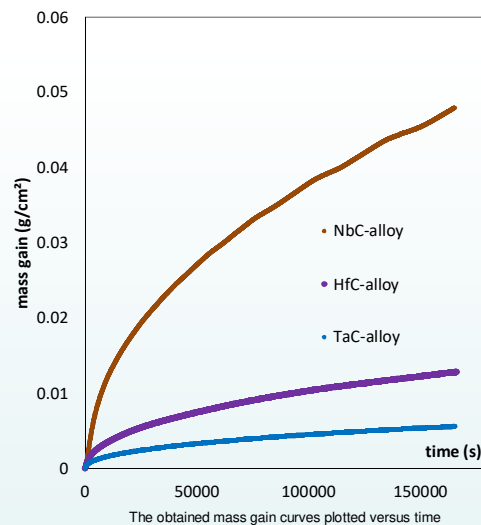
## Elaboration by high frequency induction melting, metallography and oxidation tests at 1200°C in 80%N<sub>2</sub>-20%O<sub>2</sub>



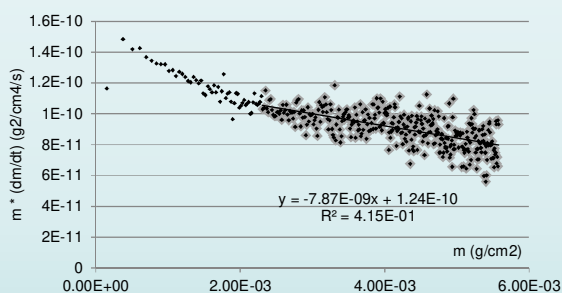
Melting of a mix of pure elements (Alfa Aesar, purity > 99.9%) using a high frequency induction furnace (CELES: operating parameters: about 150kHz, 4kV); atmosphere: 300 millibars of pure under argon



As-cast microstructures of the NbC-alloy (Co(bal.):25Cr-0.50C-3.9Nb, wt.%), of the TaC-alloy (Co(bal.):25Cr-0.50C-7.5Ta, wt.%) and of the HfC-alloy (Co(bal.):25Cr-0.50C-7.4Nb) (SEM/BSE micrographs)



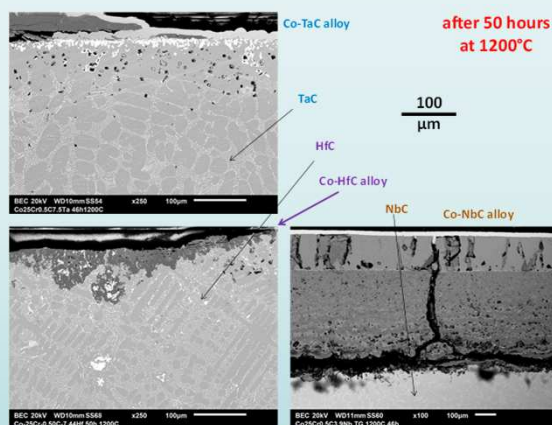
## Kinetic and metallography characterization of the oxidation behaviors



Example of treatment of the mass gain files according to the  $(m \times dm/dt = k_p - k_v \times m)$  method for extracting the values of  $k_p$  and  $k_v$  (case of the Co-TaC alloy)

The values obtained for the  $k_p$  constant classically determined (chromia volatilization not taken into account), for  $k_v$  (deduced from the  $m \times dm/dt = f(m)$  plot) and for  $k_v$

| MC-alloys with M=... | $k_p (\times 10^{-12} g^2 cm^{-4} s^{-1})$ | $k_v (\times 10^{-10} g cm^{-2} s^{-1})$ |
|----------------------|--|--|
| Nb                   | 8000                                       | 310                                      |
| Ta                   | 120  | 80                                       |
| Hf                   | 1500                                       | 800                                      |



Surface states after oxidation (cross-sectional SEM/BSE micrographs);  
**Co-TaC alloy:** outer Cr<sub>2</sub>O<sub>3</sub> continuous scale, interfacial discontinuous CrTaO<sub>4</sub> fringe and carbide-free zone; **Co-HfC alloy:** penetrating oxidation into, outer CoO oxide, spinel CoCr<sub>2</sub>O<sub>4</sub>, inner Cr<sub>2</sub>O<sub>3</sub>, no carbide-free zone but in situ oxidation the HfC into HfO<sub>2</sub>; **Co-NbC alloy:** thick external scale composed of outer CoO, CoCr<sub>2</sub>O<sub>4</sub> and inner Cr<sub>2</sub>O<sub>3</sub>, with presence of niobium oxides, deep carbide-free zone

Nb and Hf, elements able to form MC carbides well-known for their efficiency in combating creep at elevated temperatures induced obviously very low resistance against high temperature oxidation. If still considered as strengthening principle the use of these carbides supposes significant improvement in behavior of the obtained alloys: optimized chemical composition (as enrichment in chromium beyond 30 wt.% or use of protective coatings, for example). Currently, despite their moderate resistance to volume fraction lowering and to fragmentation, the carbides issued from tantalum appear as the best compromise between mechanical resistance and oxidation resistance at working temperatures as high as 1200°C.

### References:

- [1] D.Young, High Temperature Oxidation and Corrosion of Metals, Amsterdam: Elsevier Corrosion Series, 2008.
- [2] M.J.Donachie, S.J.Donachie, Superalloys: A Technical Guide, Materials Park: ASM International, 2002.
- [3] P. Berthod, Journal of Alloys and Compounds 481, 746 (2009).
- [4] P. Berthod, E. Conrath, Journal of Materials Science and Technology Research. 1, 7 (2014).
- [5] P. Berthod, Oxidation of Metals. 64(3-4), 235 (2005).