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# Microstructure evolution and oxidation behavior at high temperature of cobalt-based superalloys strengthened by hafnium carbides

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Cobalt-based superalloys elaborated by foundry are often reinforced by carbides<sup>[1]</sup>, which are generally of different types. The most common among them are chromium carbides and tantalum carbides. Unfortunately the presence of the formers generally induces for the alloy a decrease in solidus temperature while the later tend to become fragmented during high temperature exposures<sup>[2]</sup>, with consequently a loss of mechanical resistance at high temperature. Other types of carbides can be considered to strengthen such superalloys, for example hafnium carbides<sup>[3]</sup>.

In this work three HfC-reinforced chromium-rich cobalt-based alloys, Co(bal.)-25Cr-xC-yHf with (x; y)=(0.25; 3.72), (0.50; 3.72) and (0.50; 7.44) (weight contents chosen for having 1/1 and 2/1 atomic ratios between C and Hf), were elaborated by foundry and exposed at 1200°C for 50 hours to characterize their behaviours in terms of microstructure stability and of high temperature oxidation. In these fields they were compared with two Hf-free Co-25Cr-0.25&0.50C alloys subjected to the same tests.

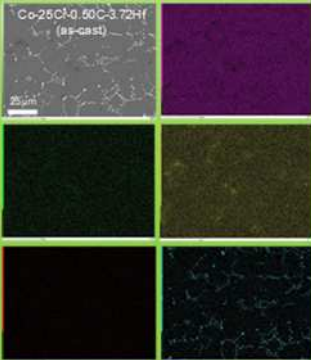
## Elaboration and microstructure examination of the alloys:

Fusion and solidification under 300mbars Ar in a High Frequency induction furnace (pure elements → ingots of 40g)



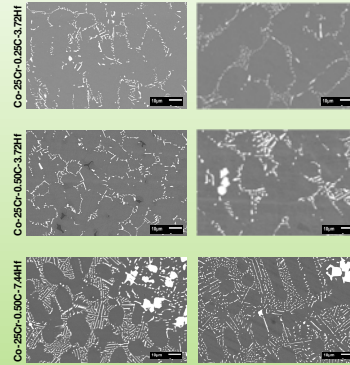
## SEM examinations, X-ray maps and XRD runs:

Dendritic matrix (fcc & hcp at room temperature)  
Hafnium carbides: compact pro-eutectic and script eutectic (mainly interdendritic)  
Rare chromium carbides in the 0.50C-3.72Hf alloy (for which at.%Hf = 1/2 at.%C)



## As-cast microstructures

Script HfC not fragmented  
More HfC if higher Hf content (no real effect of C)  
Cr carbides (rare) if ratio 2/1

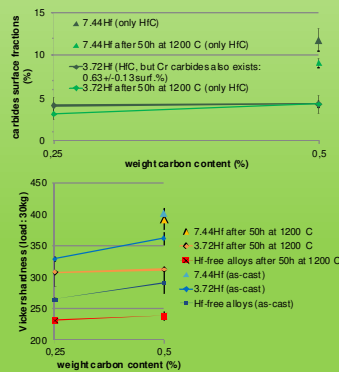


## Aged bulk microstructures

HfC a little fragmented  
Cr carbides disappeared

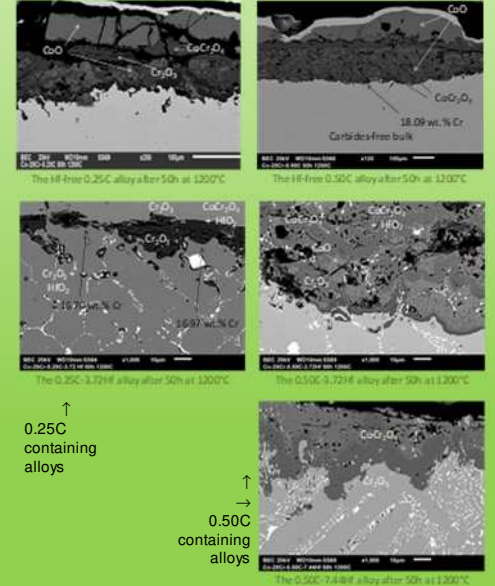
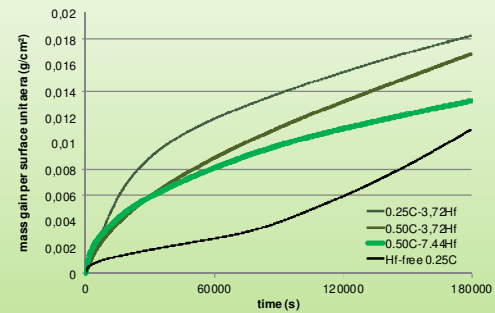
## HfC surface fractions and hardness (aged compared to as-cast)

HfC surface fraction a little decreased  
Significant decrease in hardness



## Thermogravimetry runs and post-mortem examinations:

Parabolic but fast mass gain by comparison with the Hf-free alloys\*  
Kp of about  $800 \times 10^{-12} \text{ g}^2 \text{ cm}^{-4} \text{ s}^{-1}$  (against  $30 \text{ to } 50 \times 10^{-12} \text{ g}^2 \text{ cm}^{-4} \text{ s}^{-1}$  for \*)  
Very thick multiconstituted ext. oxides (no Cr<sub>2</sub>O<sub>3</sub>-forming behaviour)  
Severe oxide spallation despite slow cooling (-5°C min<sup>-1</sup>)



Two of the three HfC-strengthened Co-based alloys studied in this work were thus successfully obtained with a dendritic matrix and an interdendritic carbides network of script eutectic HfC, thanks to an atomic ratio Hf/C equal to 1. The obtained HfC carbides were obviously slower fragmented than what it was generally observed for TaC when they are present in such quantities in other cobalt-based alloys. These observations let think that such alloys may own high mechanical properties at high temperature and notably efficient resistance against creep-deformation. In contrast their high temperature oxidation behaviour was not so good since no of them showed a chromia-forming behaviour despite their 25wt.%Cr and severe oxide spallation. Fortunately this may be improved by modifying their bulk chemical composition (e.g. increase in Cr, rare earth additions), the one of their sub-surface (e.g. by enriching it in Cr by pack-cementation) or by depositing a protective coating.

## References

- [1] Matthew J. Donachie, Stephen J. Donachie: "Superalloys: A Technical Guide", ASM International, Materials Park (2002).
- [2] Patrice Berthod, Sylvain Michon, Lionel Aranda, Stéphane Mathieu, Jean-Claude Gachon: "Experimental and thermodynamic study of the microstructure evolution in cobalt-base superalloys at high temperature", *Computer Coupling of Phase Diagrams and Thermochemistry* 27 (2003) 353-359.
- [3] Patrice Berthod, "High temperature properties of several chromium-containing Co-based alloys reinforced by different types of MC carbides (M=Ta, Nb, Hf and/or Zr)", *Journal of Alloys and Compounds* 481 (2009) 746-754.
- [4] Patrice Berthod, Elodie Conrath, "High temperature oxidation of cobalt-based alloys strengthened by hafnium carbides. Part 1: Thermogravimetry results", *Materials Science: An Indian Journal*, to be published.