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Surface states of refractory alloys rich in chromium and strengthened by different types of MC carbides after oxidation at high temperature

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❖ **How reinforcing** equiaxed cast Co-based superalloys:

- ❑ With **carbides**:
 - Generally eutectics and interdendritics
 - Thermally very stable (applications at very high temperature (T))
 - More stable than chromium carbides (Cr is necessarily present in such superalloys)
- ❑ The most stable : **tantalum carbides (TaC)**
- Often used in Co-based superalloys [1]

❖ **Research of new carbides**:

- ❑ More stable than TaC:

- ❑ To limit the carbides \searrow and fragmentation [2]
- ❑ To limit the \searrow of the thermo-mechanical properties of superalloys [3,4]

❖ **Study of hafnium carbides (HfC)**:

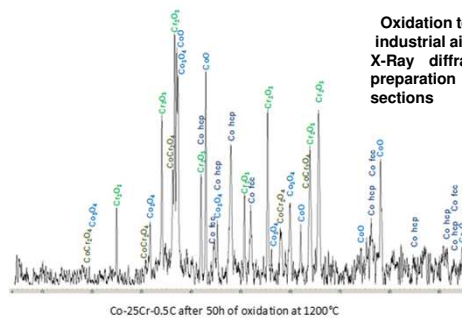
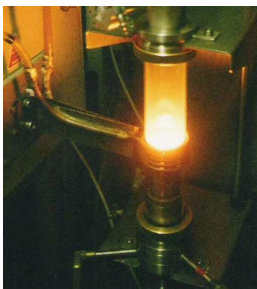
- ❑ Crystallize as pro-eutectic compact HfC [5] and script-like carbides too [6]
- ❑ Better stability than TaC at very high temperature [7, 8]
- ❑ Hf known to be good for resistance to high T oxidation [9, 10]
- ❑ But, in so high quantities: risks of becoming detrimental for the resistance against the high T oxidation \rightarrow point to verify

❖ **In a parallel work** [11]:

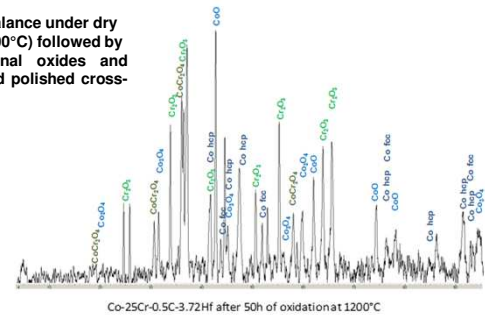
- ❑ 3 Co-based quaternary alloys with Hf (Co-25Cr-0.25C-3.72Hf ; Co-25Cr-0.5C-3.72Hf and Co-25Cr-0.5C-7.44Hf) and 2 Co-based ternary alloys (Co-25Cr-0.25C and Co-25Cr-0.5C):
 - Cast by High Frequency induction melting
 - Tested in oxidation in thermo-balance (50h, 1200°C):
 - To characterize the oxidation kinetic
- ❖ **The purpose of this work**:
 - ❑ Post-mortem characterization after high T oxidation
 - ❑ Better understanding of the differences of kinetic between the HfC-containing alloys and the ternary ones:
 - ❑ Comparison with similar Ni-based alloys

Elaboration :

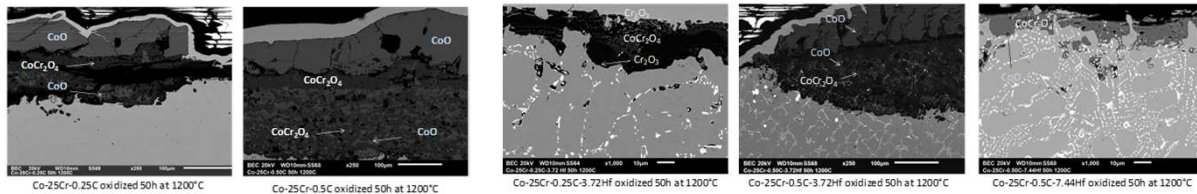
Fusion and solidification under 300mbars Ar in a High Frequency induction furnace (pure elements \rightarrow ingots of 40g)



Oxidation tests in thermo-balance under dry industrial air (50 hours at 1200°C) followed by X-Ray diffraction on external and preparation of embedded and polished cross-sections



Scanning Electron Microscope (SEM) micrographs taken in Back Scattered Electrons mode (BSE) illustrating the oxidized surfaces and deteriorated subsurfaces



Energy Dispersion Spectrometry (EDS) results for identifying the external and internal oxides and to value the decrease in chromium content in extreme surface

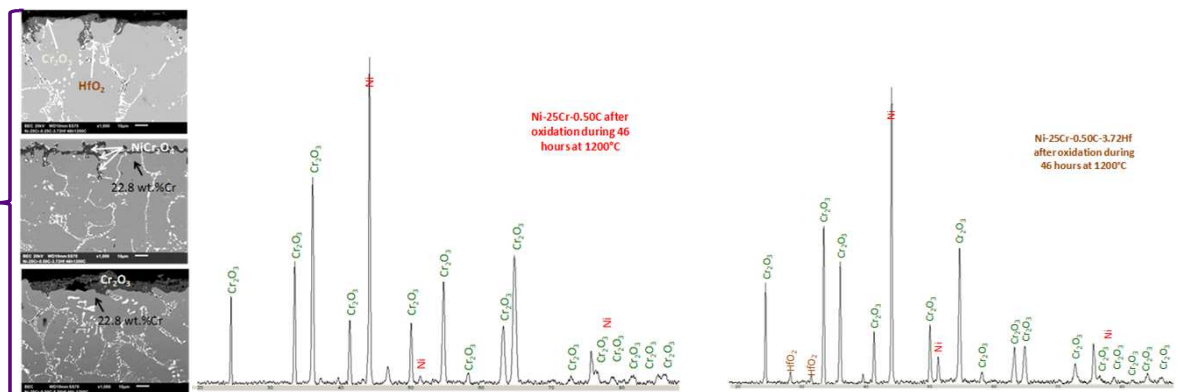
General – or at least local – catastrophic oxidation: presence of thick scales, composed of complex oxides...

Examples of chromium contents determined in extreme surface by EDS measurements:

18.1wt.%Cr in the Co-25Cr-0.50C alloy
16.7wt.%Cr in the Co-25Cr-0.25C-3.72Hf alloy

Comparison with the same results obtained on ternary and Hf-rich nickel based alloys elaborated following the same elaboration route and oxidized for 46 hours at 1200°C:

Much better behavior for the Ni-based alloys, ternary or Hf-rich ones: all chromia-forming behavior, higher Cr contents in extreme surface



❖ All the **Co-based alloys**:

- ❑ Affected by catastrophic oxidation:
 - Confirmed by the metallographic characterizations
 - Contrarily to the Ni-based corresponding alloys (chromia-forming behavior conserved)

❖ **Catastrophic oxidation**:

- ❑ Appears early for the quaternary alloys:
 - Fast parabolic kinetics
 - Very high final mass gain

❖ **Problems with the $\{m.(dm/dt) = Kp - Kv.m\}$ method:**

- To extract correct Kp and Kv values
- Because not only Cr₂O₃ in the oxide scale

❖ **Behavior in high T oxidation:**

- ❑ Not good at 1200°C: no great resistance against oxidation at high T
- ❑ Worse for the quaternary alloys than for the ternary ones

❖ **Several solutions:**

- ❑ \nearrow the Cr content:
 - Up to 30 wt.%Cr
 - In order to have more than 15 wt.% on extreme surface
- ❑ Adding more Hf:
 - To form not only HfC carbides and to have free Hf atoms in the matrix
 - Hf maybe able to diffuse to the oxidation front:
 - Improve the oxidation behavior
 - Better adherence of the oxide scales

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