

Comportement en oxydation, à 1000°C et plus, de l'alliage de Cantor et de quelques alliages dérivés

Behavior in oxidation, at 1000°C and more, of the Cantor's alloy and of several derived versions

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Introduction

Hot oxidation of the Cantor's alloy and of its MC–strengthened versions

Hot oxidation of {low Mn–high Cr} versions of these alloys

Conclusions

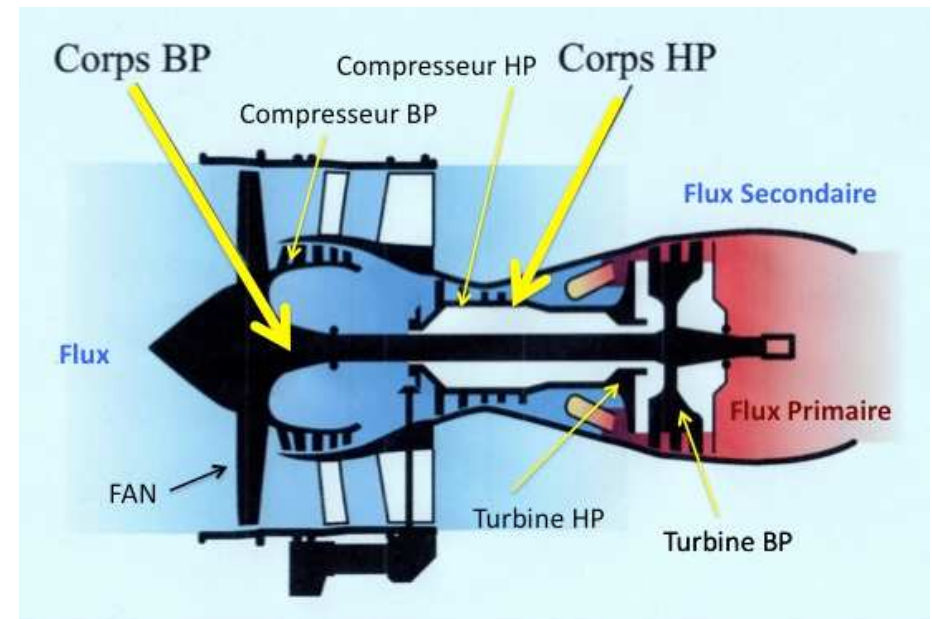
Introduction

Service at high temperatures

- * examples of components turbine disks and blades, combustion chamber...
- * severe mechanical and chemical solicitations



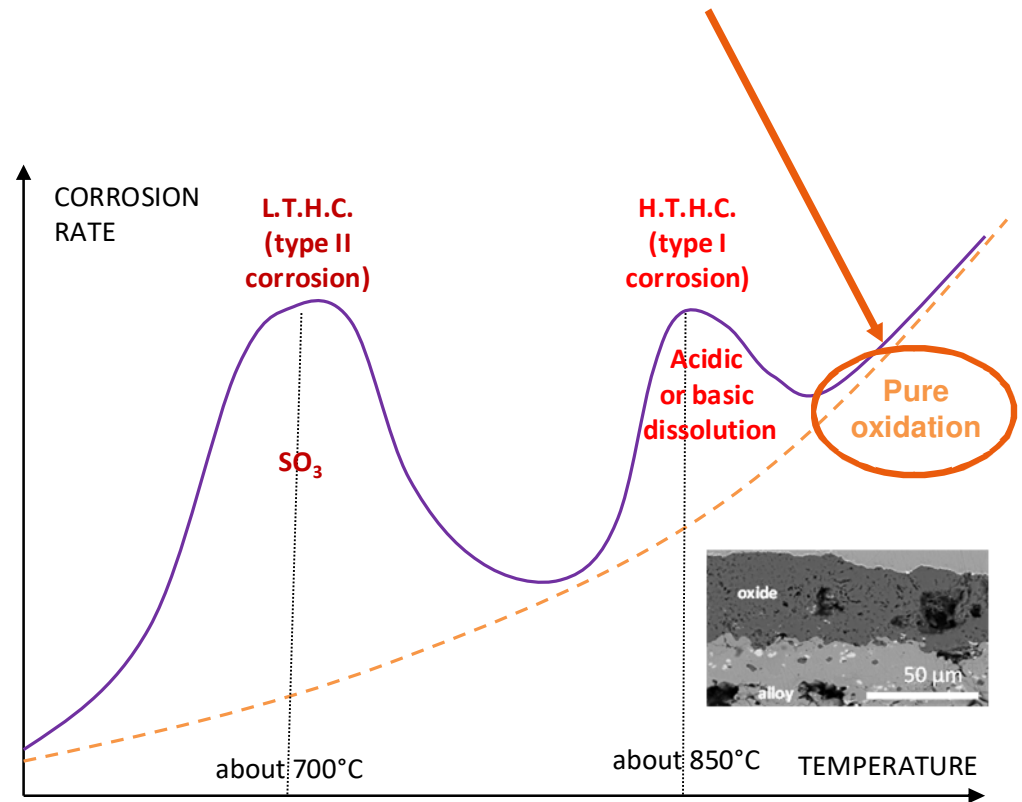
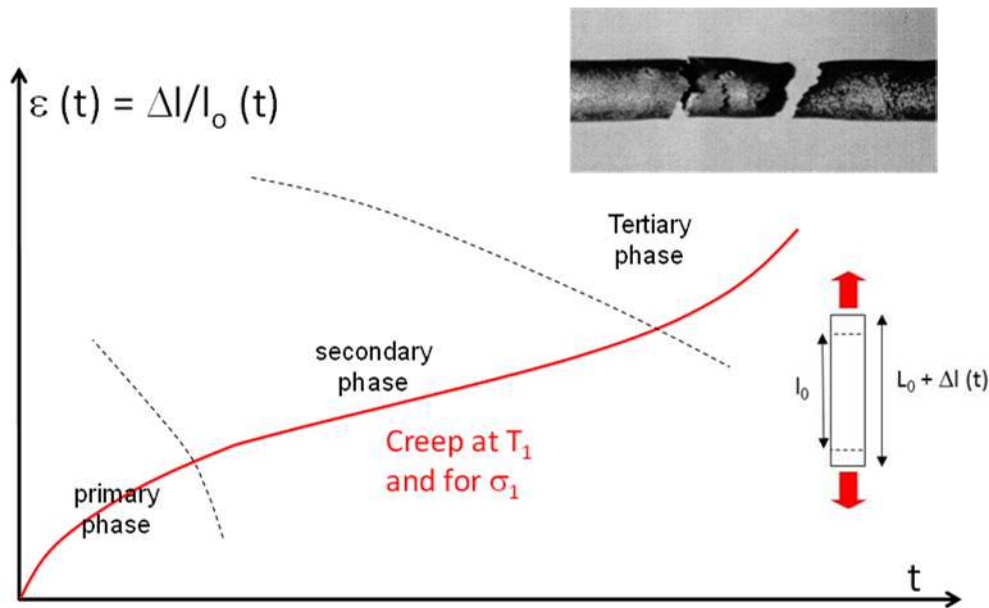
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Properties needed at high temperature ($T > 1000^\circ\text{C}$):

good resistances against thermal fatigue, creep... and corrosion by melts, OXIDATION BY GASES AT HIGH TEMPERATURE

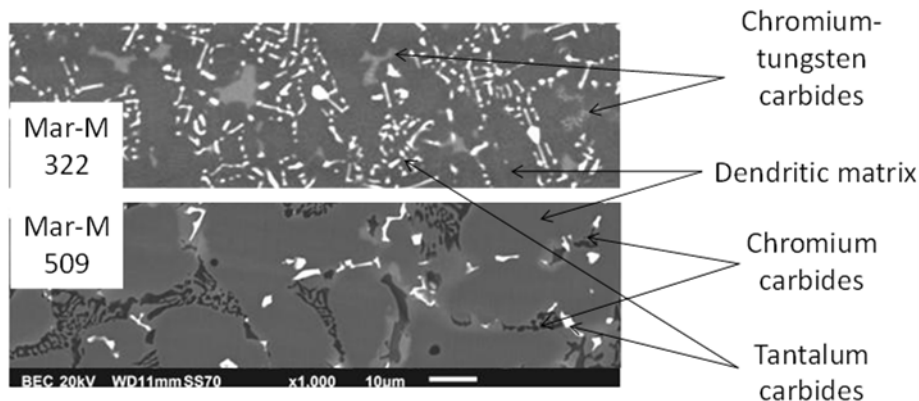


→ Superalloys (metallic alloys with exceptional properties)

* Example 1: γ/γ' single crystalline superalloys

(limited to 1100°C because of γ' dissolution problems)

* Example 2: polycrystalline cast superalloys strengthened by carbides



* Most of them: based on nickel and cobalt

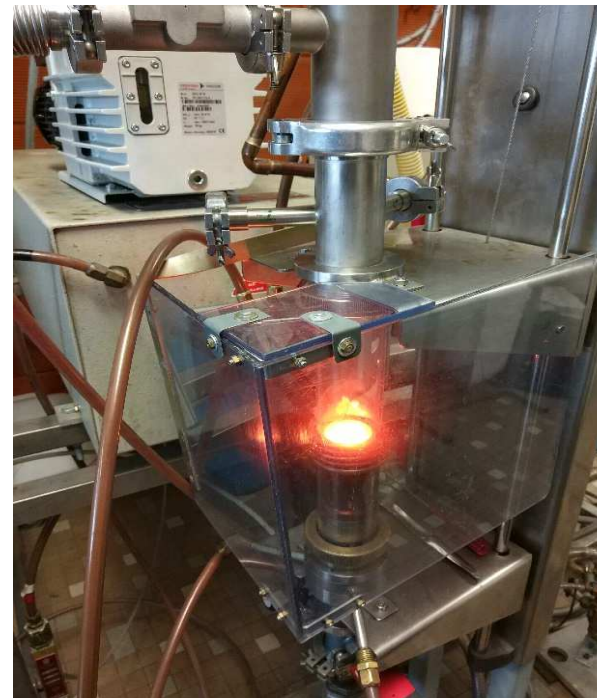
* Being less dependent on Ni and Co
→ partial substitution by Fe and Mn

i.e. → based on the Cantor's alloy
(equimolar CoNiFeMnCr High Entropy Alloy)

Hot oxidation of the Cantor's alloy and of its MC–strengthened versions

Elaboration of the alloys for the study

- Chemical compositions:
 - Co-Ni-Fe-Mn-Cr (20 at.% each)
 - 0.25C-3.8Ta–CoNiFeMnCr (bal.)
 - 0.25C-3.7Hf–CoNiFeMnCr (bal.)
- 40g of mix of pure elements (>99.9%)
- High frequency induction furnace
- 300 millibars pure Argon
- 10 minutes of homogenization in the liquid state ($\approx 1700^{\circ}\text{C}$)



Chemical compositions

- MC-free version: targeted composition well respected
- MC – containing versions:

TaC-alloy	Co	Ni	Fe	Mn	Cr	Ta
General	19.3	20.1	18.6	18.3	19.2	4.5
Wt.%	0.2	0.5	0.5	0.3	0.3	0.4
Matrix	20.5	20.5	20.9	16.7	19.4	2.1
Wt.%	0.4	0.3	0.9	1.4	0.6	0.1

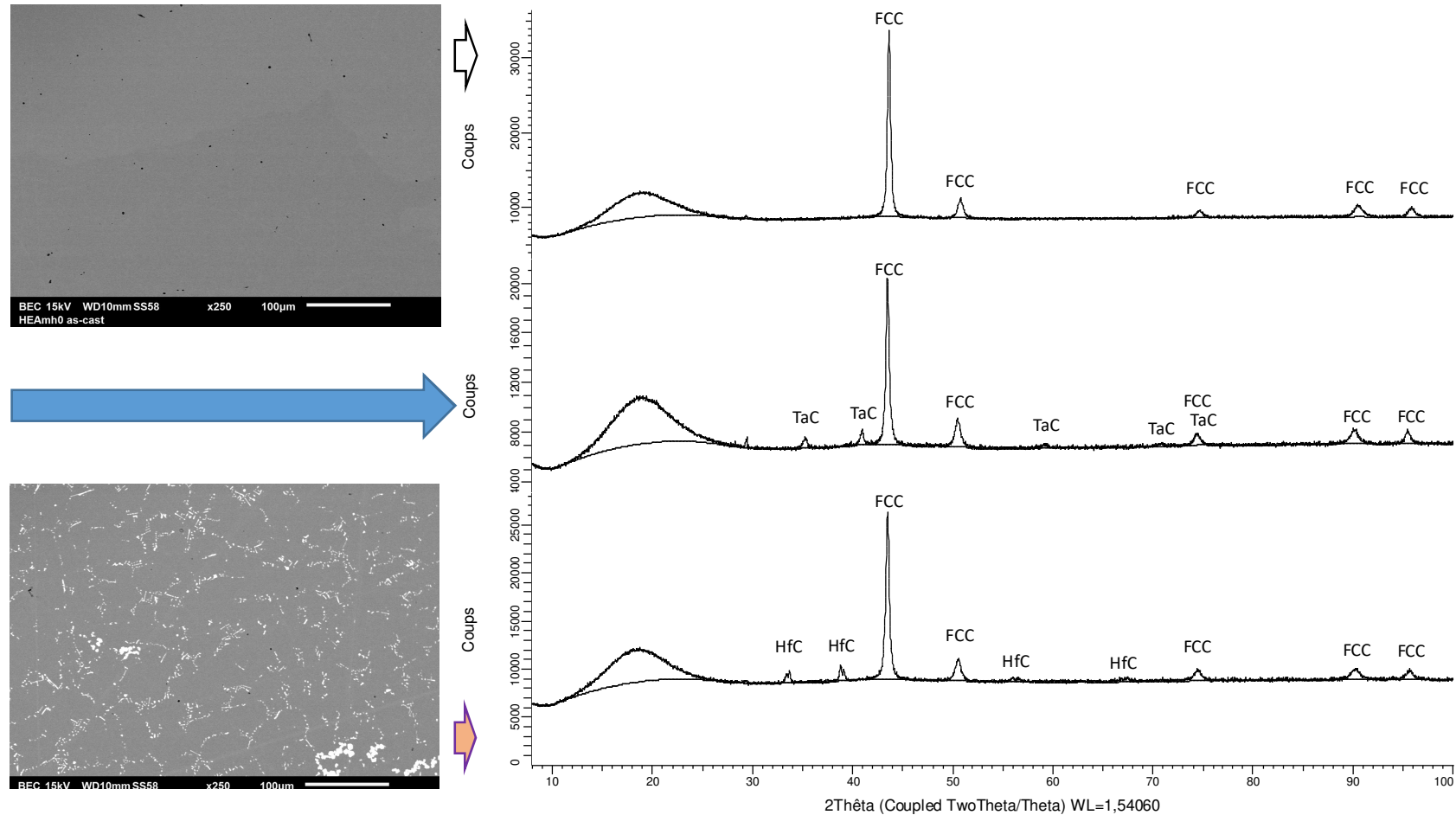
+ 0.25 Wt.% C

HfC-alloy	Co	Ni	Fe	Mn	Cr	Hf
General	19.9	20.2	18.4	18.2	19.3	4
Wt.%	0.3	0.6	0.4	0.2	0.5	1.9
Matrix	21.1	19.7	21.6	16.8	20.7	0.1
Wt.%	1.2	0.7	1.6	1.8	0.3	0.1

+ 0.25 Wt.% C

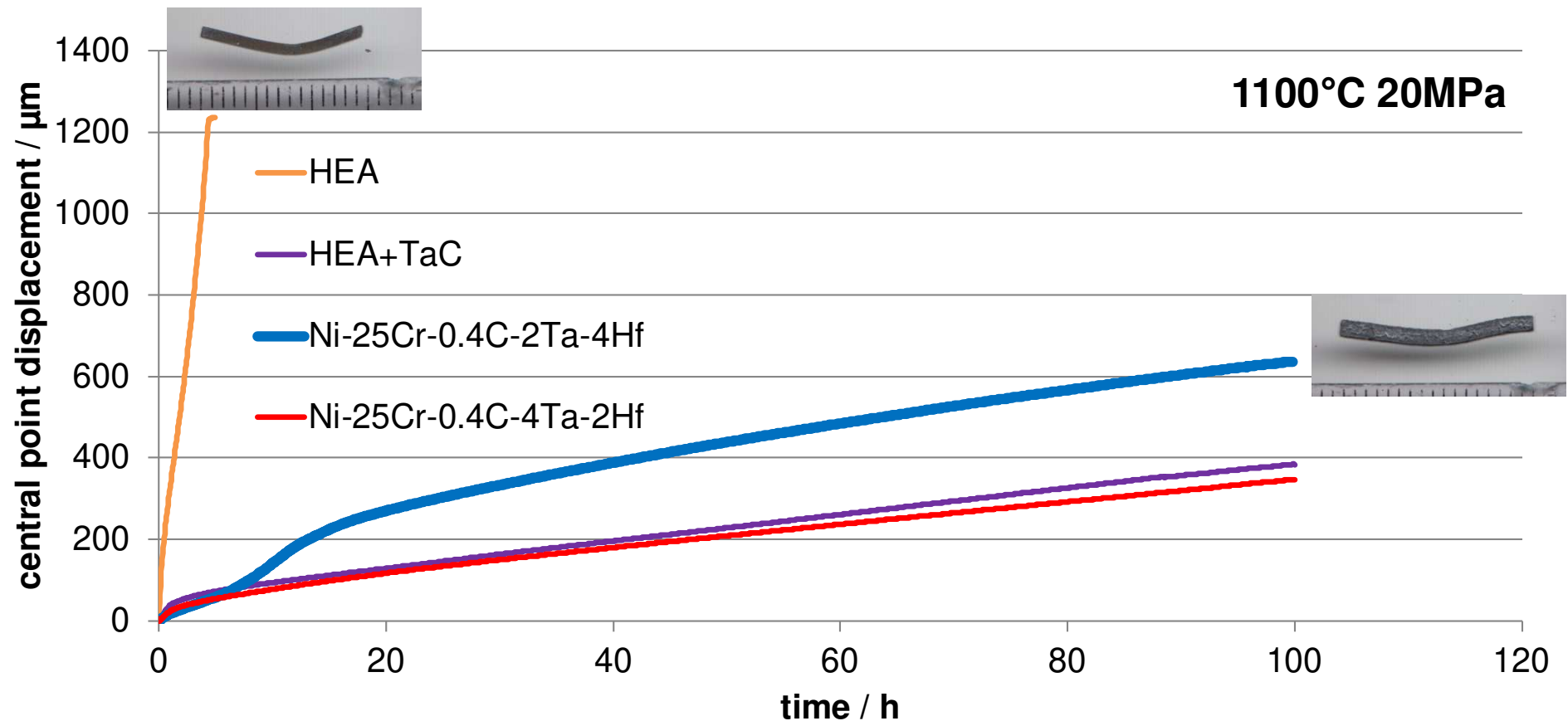
Microstructures

- MC-free version: single-phased (FCC)
- MC-containing versions: the previous one + TaC or HfC



Control of the creep properties (3 pts flexural)

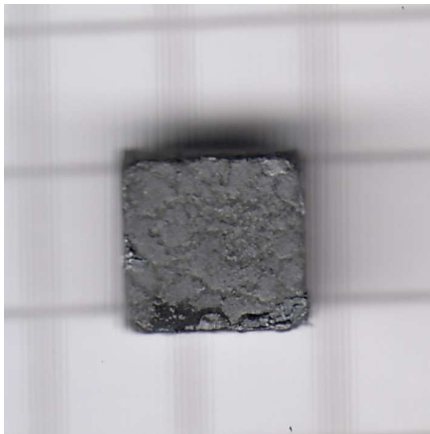
- **MC-free version: fast deformation**
- **MC-containing versions: much better resistance** (for the TaC version → comparable to MC-strengthened Ni(Cr)-based alloys)



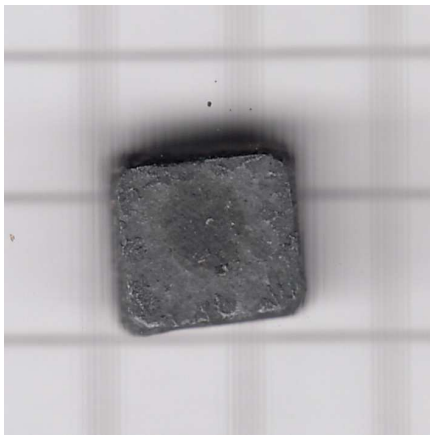
High temperature oxidation of the MC–HEAs

- Preliminary tests: 50h at 1000°C & 1100°C in furnace (ambient air)
- Tendency to oxide scale spallation

Cantor's alloy

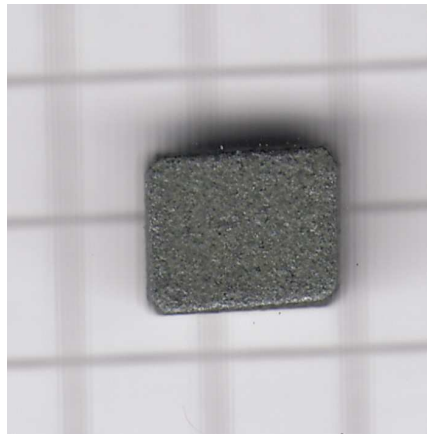


50h@1100°C

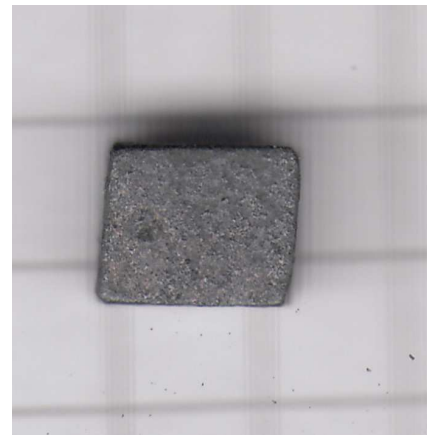


50h@1000°C

TaC–containing Cantor's alloy

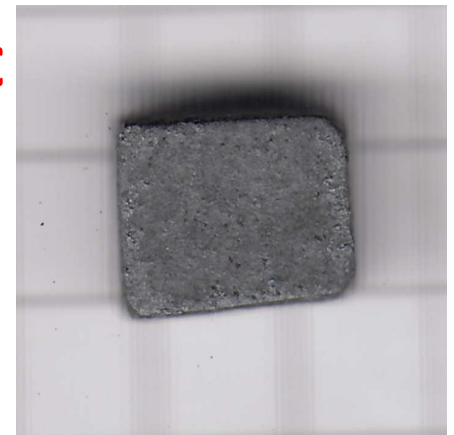
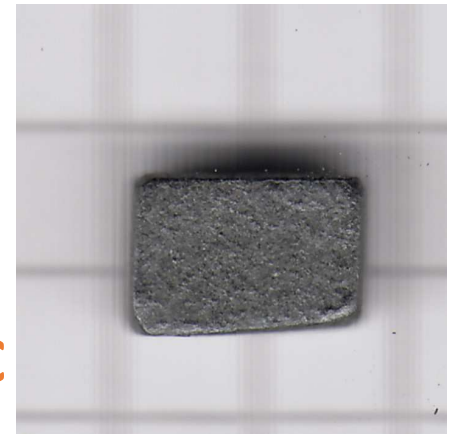


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50h@1000°C

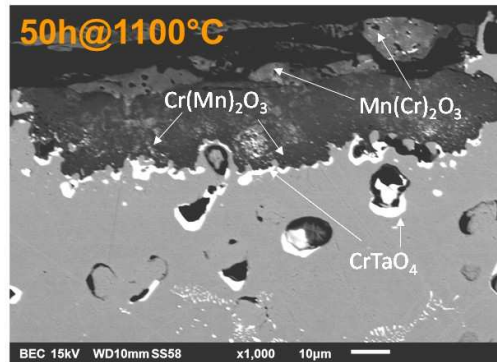
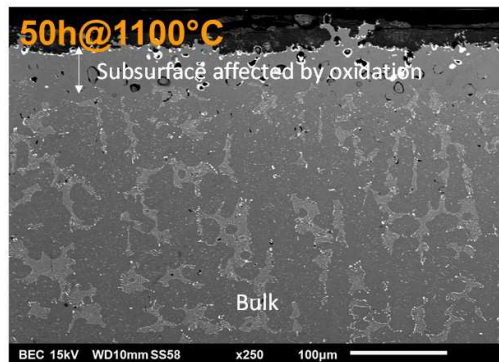
HfC–containing Cantor's alloy



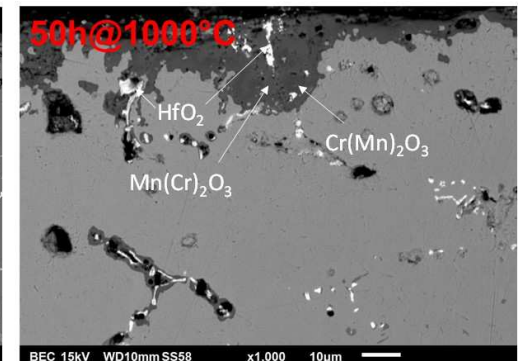
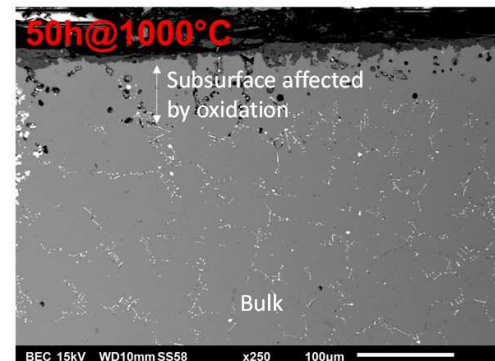
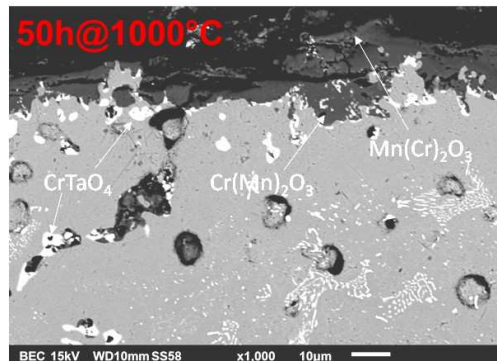
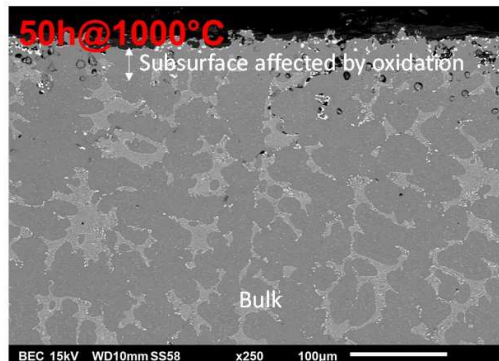
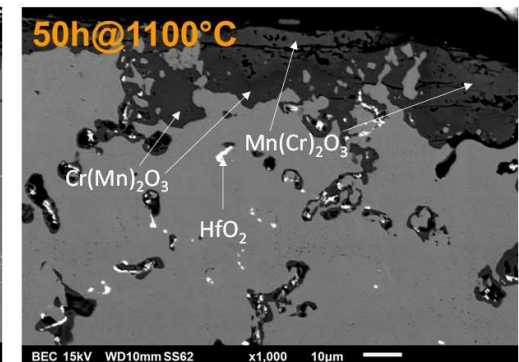
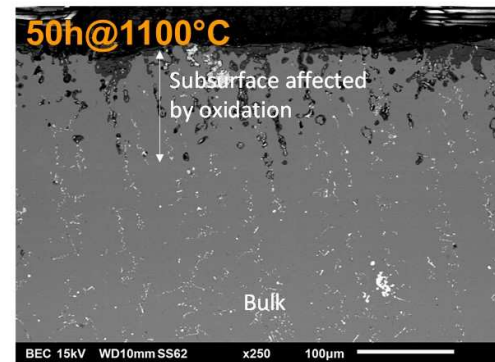
High temperature oxidation of the MC–HEAs

- The three alloys: thick external scale of {Mn, Cr}–oxides
- MC–containing ones: ... + internal oxidation of Ta and Hf

TaC–containing Cantor's alloy

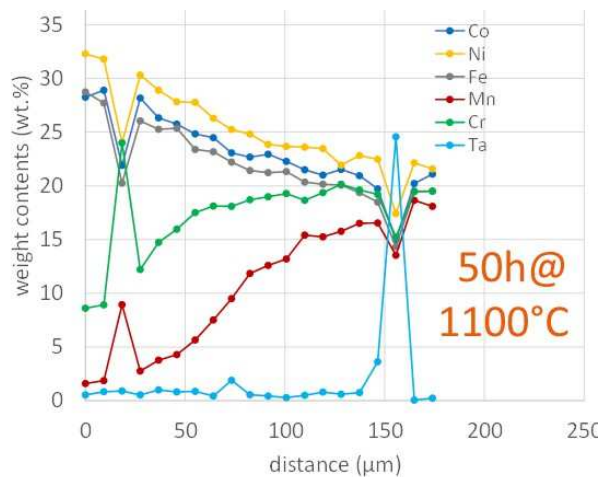


HfC–containing Cantor's alloy



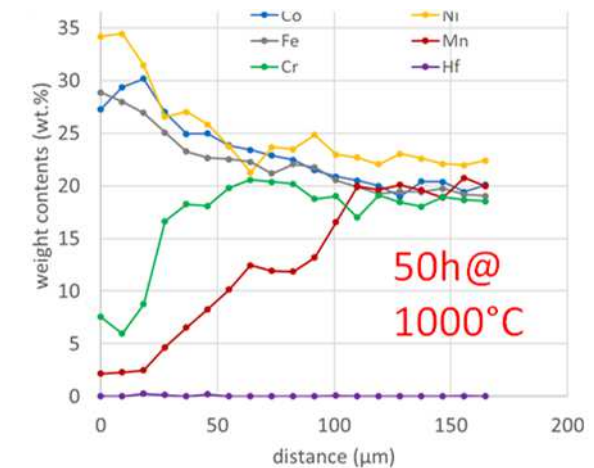
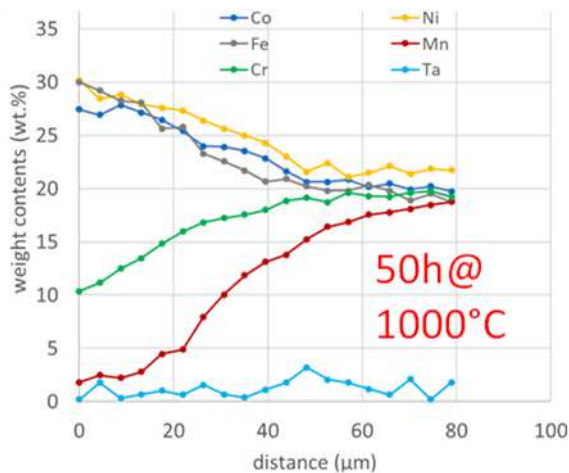
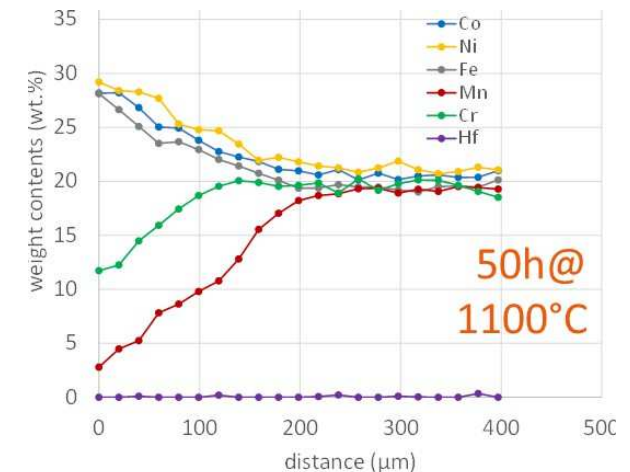
High temperature oxidation of the MC–HEAs

- Mn much more involved by oxidation than Cr
- Metallographic deduction of Kp: much faster oxidation than chromia-forming alloys (7 times higher for both temperatures)



TaC-containing
Cantor's alloy

HfC-containing
Cantor's alloy



Intermediate conclusion

- Predominant role of Mn; it masks chromium oxidation and obstructs the development of a protective chromia layer
- Complexity of the formed $\{z\text{Mn}, (1-z)\text{Cr}\}_x\text{O}_y$ external scale (z, x and y varying perpendicularly to the scale/alloy interface); obviously less protective than chromia
- Too fast oxidation to take benefit from the interesting creep resistance of the MC-containing versions
- Improving the oxidation resistance is compulsory
- This can be done by decreasing the Mn content; Cr increase can be also relevant

Hot oxidation of {low Mn–high Cr} versions of the previous alloys

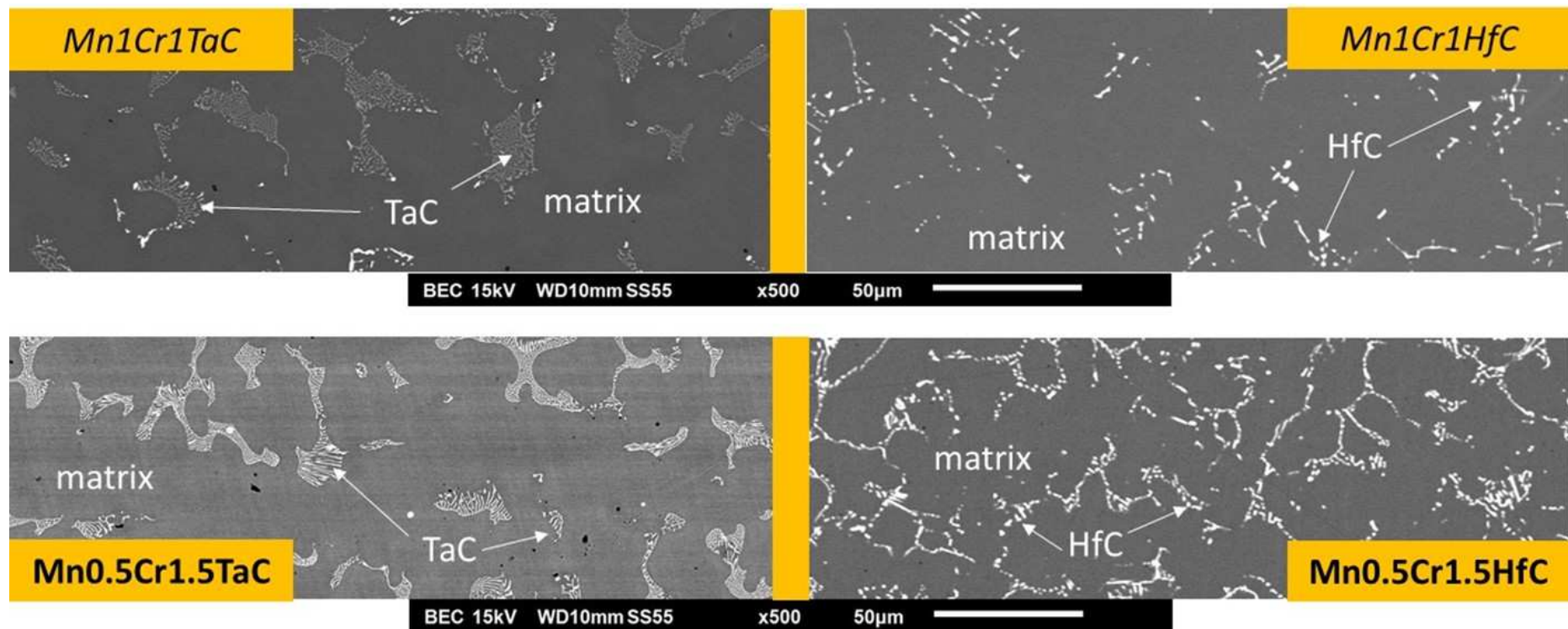
New targeted compositions:

- 20 at.%Co – 20 at.%Ni – 20 at.%Fe – ~~20~~ 10 at.%Mn – ~~20~~ 30at.%Cr
- The same + 0.25 wt.%C – 3.8 wt.%Ta
- The same + 0.25 wt.%C – 3.7 wt.%Hf
- Obtained compositions (SEM/EDS) ↓

Alloys ↓	Co	Ni	Fe	Mn	Cr	Ta	Hf	C
<i>Mn1Cr1</i>	20.0 ±0.5	21.5 ±0.5	19.5 ±0.5	19.5 ±0.5	20.5 ±0.5	/	/	/
➔ Mn0.5Cr1.5	20.0 ±0.1	20.5 ±0.3	19.8 ±0.2	8.3 ±0.5	31.3 ±0.4	/	/	/
<i>Mn1Cr1TaC</i>	19.3 ±0.2	20.1 ±0.5	18.6 ±0.5	18.3 ±0.3	19.2 ±0.3	4.5 ±0.4	/	0.25
➔ Mn0.5Cr1.5TaC	19.5 ±0.2	20 ±0.5	19.1 ±0.3	8.4 ±0.2	28.5 ±0.3	4.6 ±0.2	/	0.25
<i>Mn1Cr1HfC</i>	19.9 ±0.3	20.2 ±0.6	18.4 ±0.4	18.2 ±0.2	19.3 ±0.5	/	4 ±1.9	0.25
➔ Mn0.5Cr1.5HfC	19.7 ±0.4	20.1 ±0.3	19.1 ±0.3	8.8 ±0.3	27.8 ±0.7	/	4.5 ±0.6	0.25

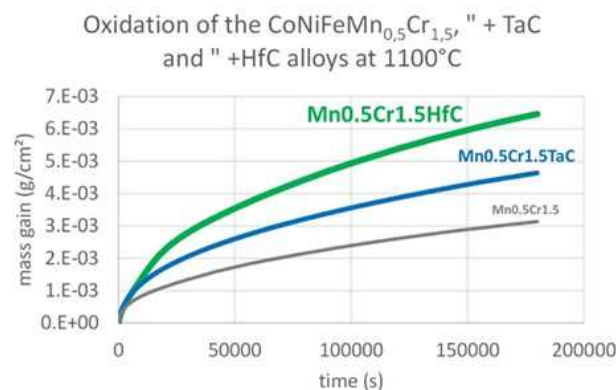
Microstructures and creep behaviors:

- $\text{CoNiFeMn}_{0.5}\text{Cr}_{1.5}$: single-phased FCC, as the equimolar alloy
- MC-cont^a low Mn high Cr alloys: double-phased FCC + MC
- Creep: similar to the equimolar MC-free and MC-cont^a versions

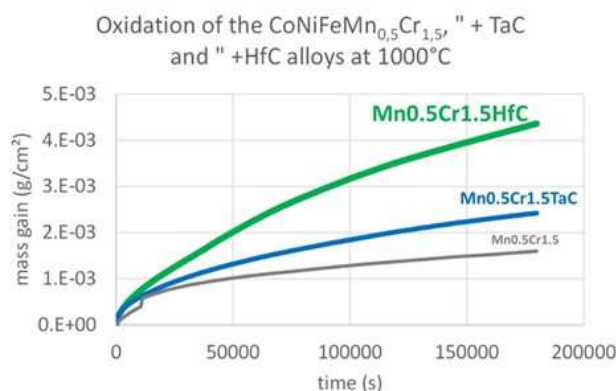


Hot oxidation in thermo-balance (80%N₂–20%O₂):

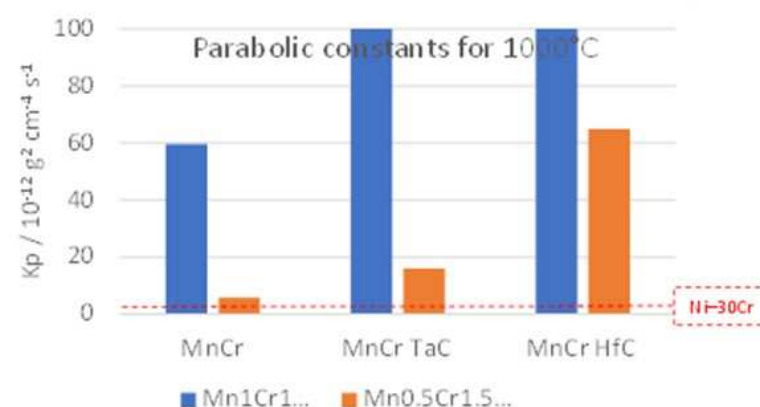
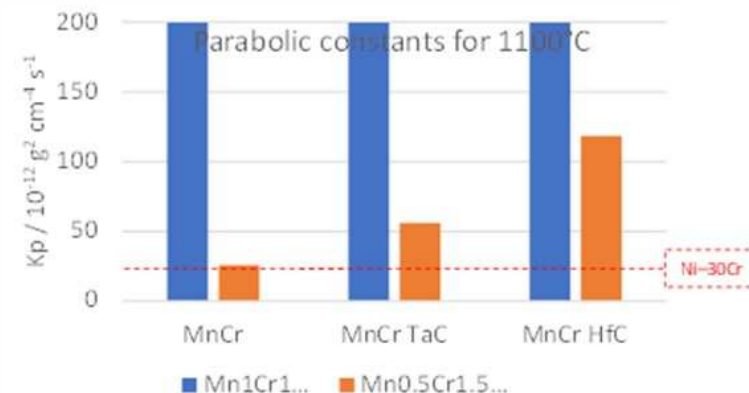
- Kinetics parabolic again
- Low Mn – high Cr alloys: K_p much decreased / Cantor–based
- MC–ct⁹ lowMn–highCr alloys: faster oxidation / CoNiFeMn_{0.5}Cr_{1.5}



50h@1100°C

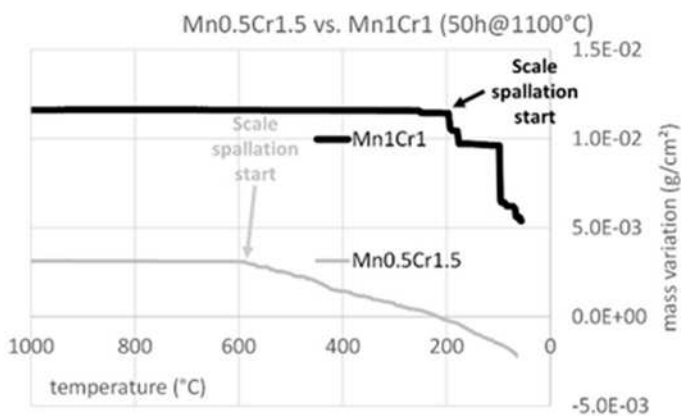


50h@1000°C

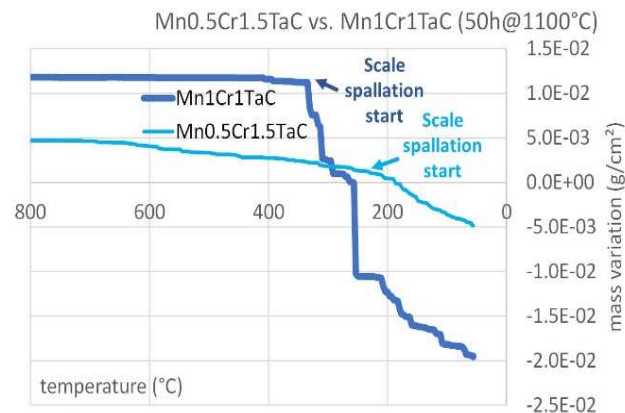


Hot oxidation in thermo-balance (80%N₂–20%O₂):

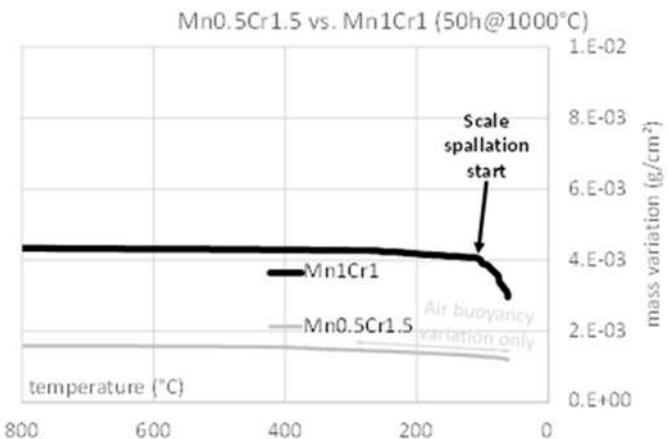
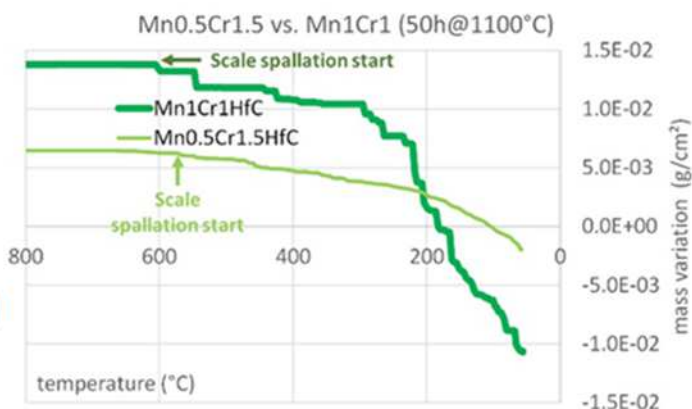
- 1100°C: oxide scale spallation more severe than for 1000°C
- Low Mn–high Cr alloys more resistant against scale spallation than the CoNiFeMnCr–based alloys; deleterious effect of MC



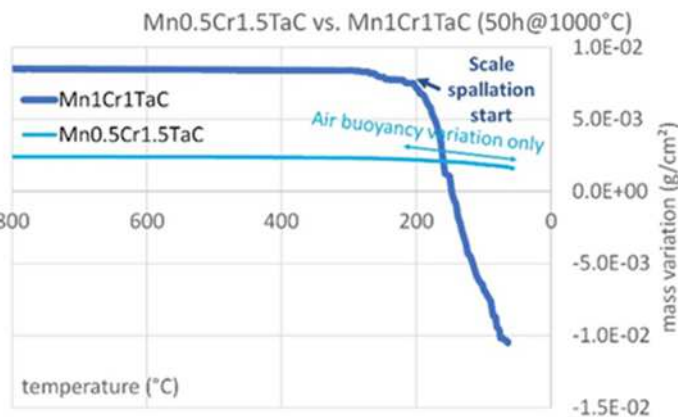
50h@1100°C



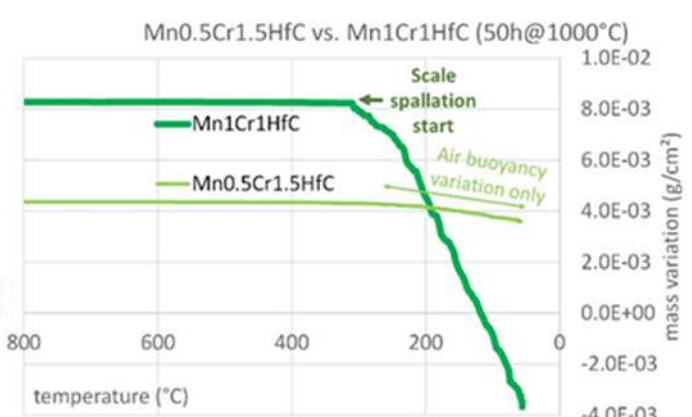
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50h@1000°C

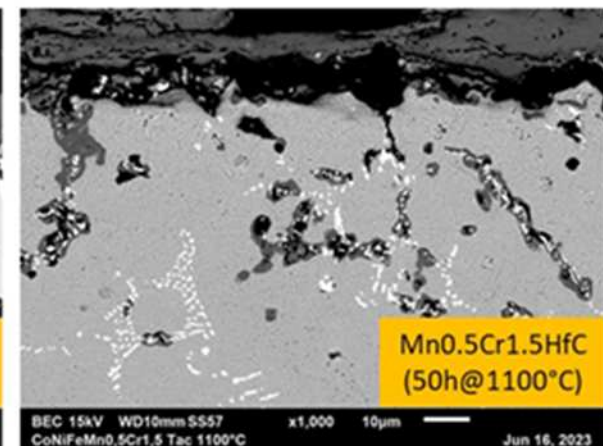
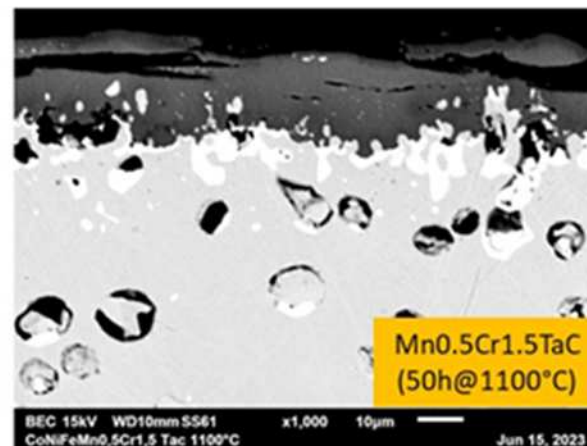
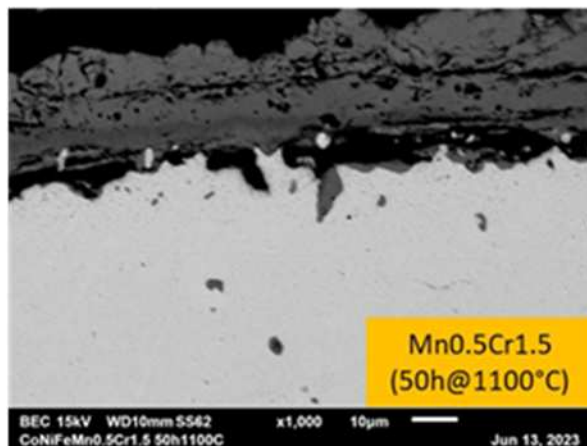
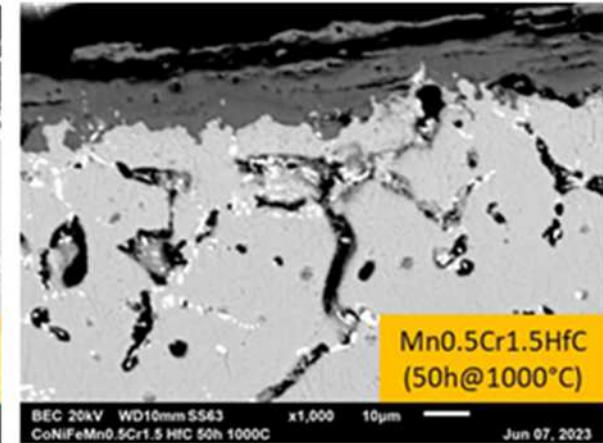
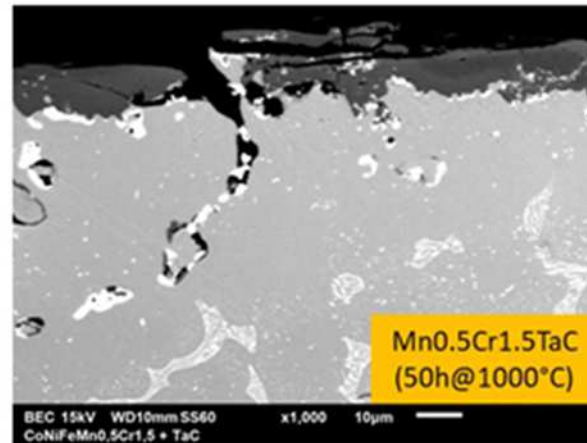
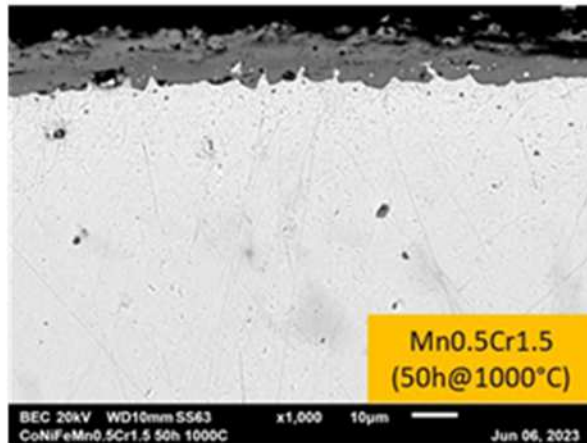


50h@1000°C



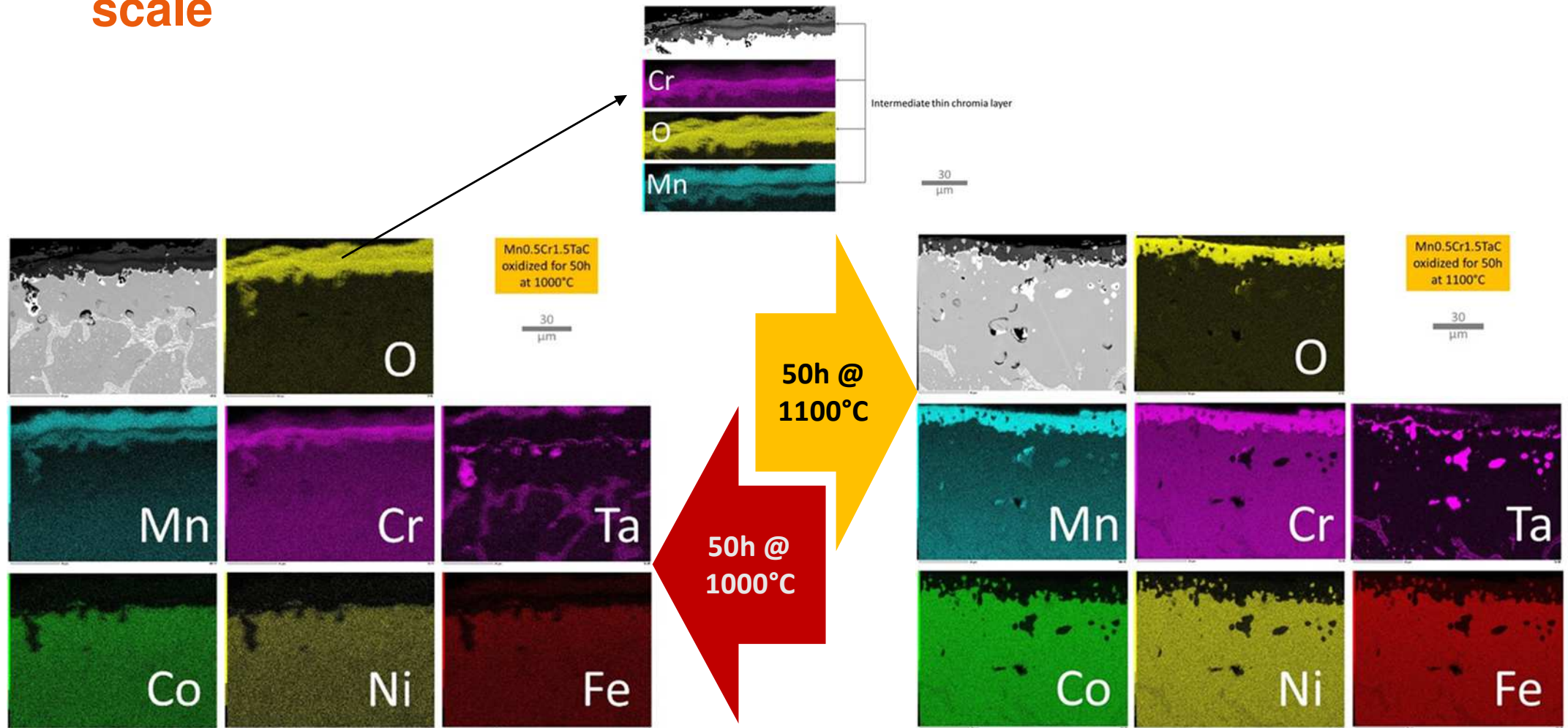
Post-mortem cross-sectional observations

- Oxide scales better kept than for the Cantor-based alloys
- Mn more involved by oxidation than Cr, again, although $\text{Mn} \ll \text{Cr}$ in the new versions



Post-mortem cross-sectional observations

- Multi-constituted again, variations in Mn and in Cr
- Presence of an internal continuous chromia layer in the scale



Conclusions

- **Equimolar Cantor's and derivative alloys: low resistance in oxidation at 1000°C and beyond**
 - **But ↓ Mn and ↑ Cr indisputably improve their behavior**
 - **However, these low Mn–High Cr are still below a Ni–30Cr**
 - **MC carbides are efficient to slow down creep rates but degrade oxidation resistance (especially HfC)**
- Removing all Mn and testing CoNiFeCr + MC alloys?
(MPEAs at the {Cantor / Co-based/Ni-based alloys} border)
- Protective coatings?

Remerciements

À mes collègues

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