

Behavior in cooling–induced oxide scale spallation of original and modified Cantor’s HEA alloys oxidized at high temperature

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About the Presenter

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CV highlights and research interests:

- **Mech. Eng. Ecole Centrale de Lille, PhD Mater. Sci., Habil. Chemistry**
- **Foundry, metallurgy, corrosion, microstructures and properties of superalloys at high temperature**

“Surface & Interface: Chemical Reactivity of Materials” research group

Work achieved without funding sources

No conflict of interest

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Outlines

- **Introduction**
- **Short reminder about the synthesis route, and the obtained chemical compositions and microstructures**
- **Oxide scale spallation during post–isothermal oxidation cooling**
 - Oxidized samples observed by the naked eye
 - Exploitation of the cooling parts of the thermogravimetry curves
 - Cross–sectional observations
- **Conclusions**
- **Outlooks**



Introduction

- High Entropy Alloys; equimolar CoNiFeMnCr composition: Cantor Alloy
- Adding MC carbides → increase in mechanical resistance at H.T.
- Isothermal oxidation behavior at 1000°C and 1100°C (*shown today, at 2:20 PM*)
 - Mass gain kinetic: parabolic but ...
 - Very fast for the Cantor alloys and its {+MC} derivatives
 - Slowed down if ↓ Mn to 10 at.% and ↑ Cr to 30 at.% (*but still worse than Ni–30 wt.%Cr*)
- More or less protection by the external multi-constituted oxide scale
- **THIS WORK: how does this complex scale behave if temperature varies?**
→ first answers available in the cooling parts of the thermogravimetry curves



Reminder about the synthesis route

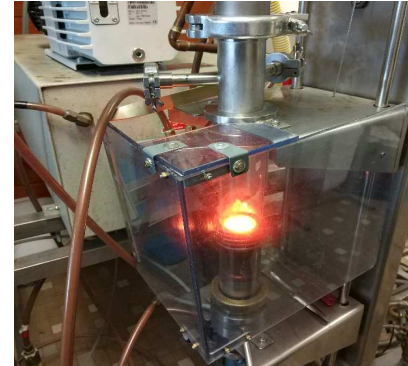
- **Targeted chemical compositions:**

Common parts: Co-Ni-Fe-Mn-Cr (20 at.% each) or CoNiFe-**10at.%Mn- 30at.%Cr**

- No more elements
- or + 0.25C-3.8Ta (wt.%)
- or + 0.25C-3.7Hf (wt.%)

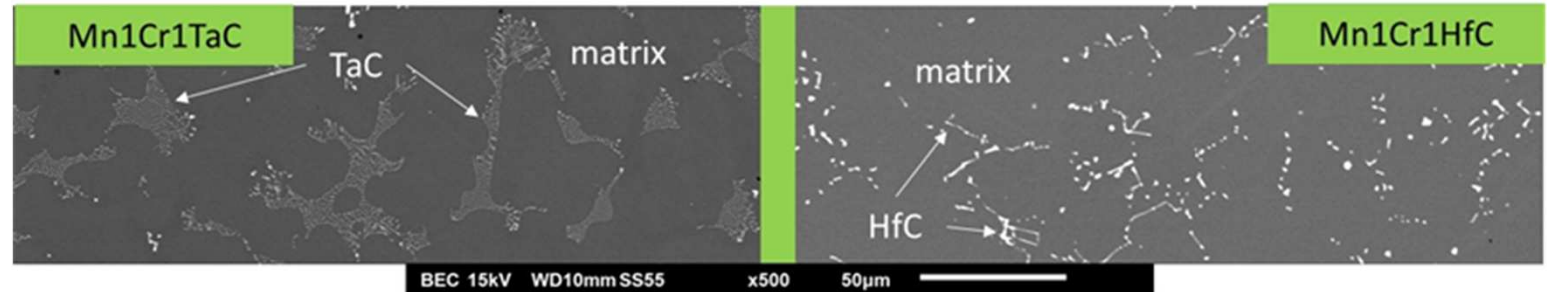
- **Technical details:**

- 40g of mix of pure elements (>99.9%)
- High frequency induction furnace, 300 millibars pure Argon
- Melting in the water-cooled copper crucible (5kV, 110kHz)
- 10' of homogenization in the liquid state ($\approx 1700^{\circ}\text{C}$), solidification and cooling

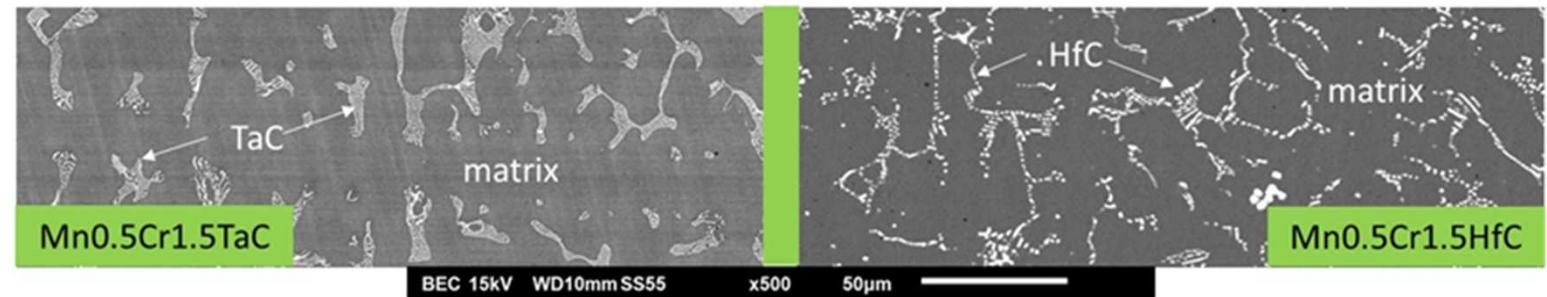


Reminder of the alloys characteristics

equimolar-based alloys



modified alloys

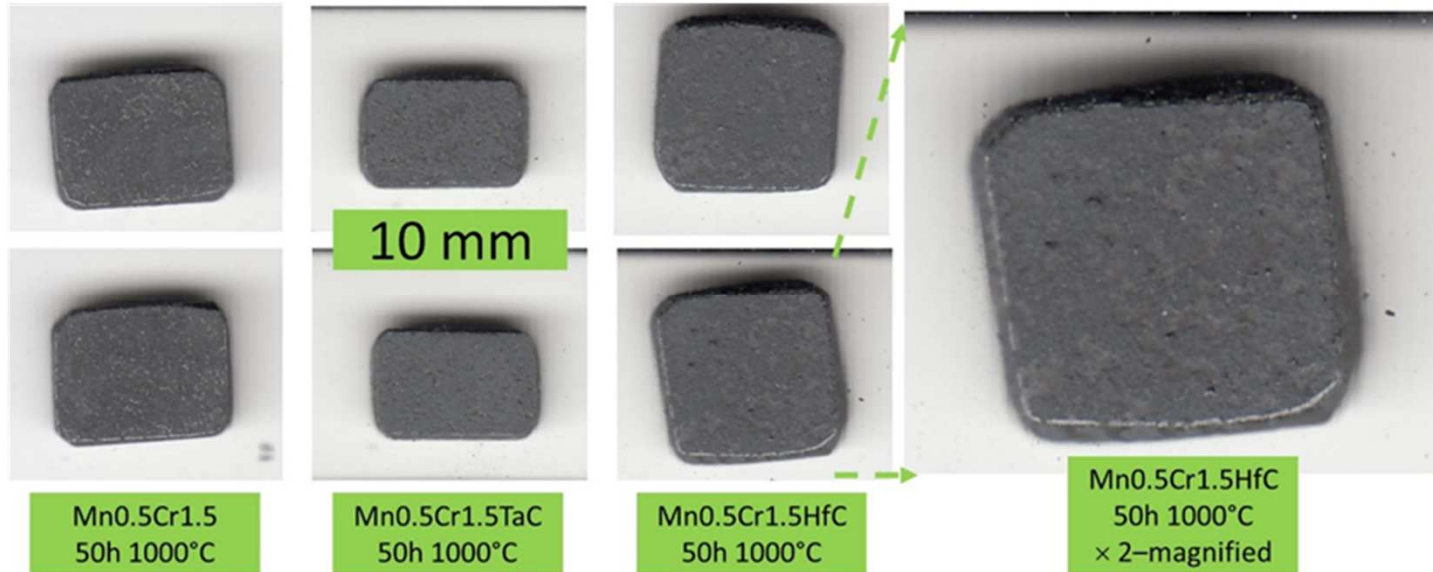


- Obtained chemical compositions: close to the targeted ones
- Dendritic matrix and eutectic carbides (and some pre-eutectic HfC)



Oxide scale spallation behavior

Oxidized samples observed by the naked eye

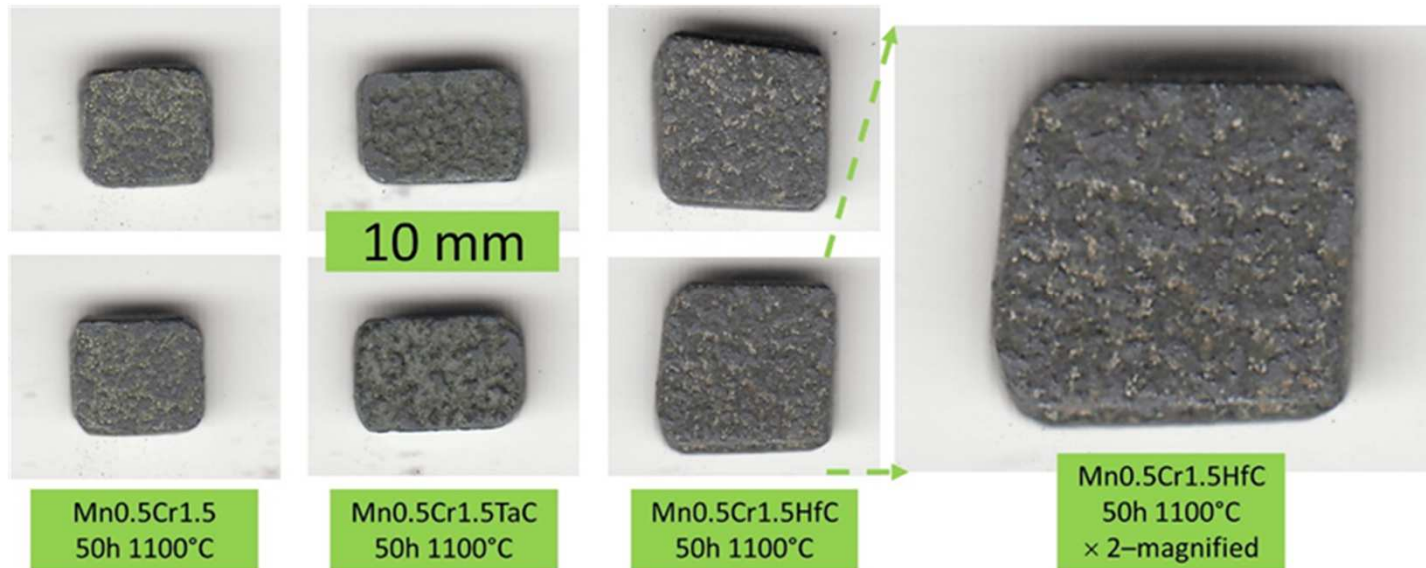


Cooling at -5 K min⁻¹ from 1000°C

- Reminder of the mass gain isothermally achieved:
≈ 1.6 mg / cm² for Mn_{0.5}Cr_{1.5}, 2.4 mg / cm² (+TaC), 4.3 mg / cm² (+HfC)
- No evident oxide scale loss, except along the edges and corners

Oxide scale spallation behavior

Oxidized samples observed by the naked eye

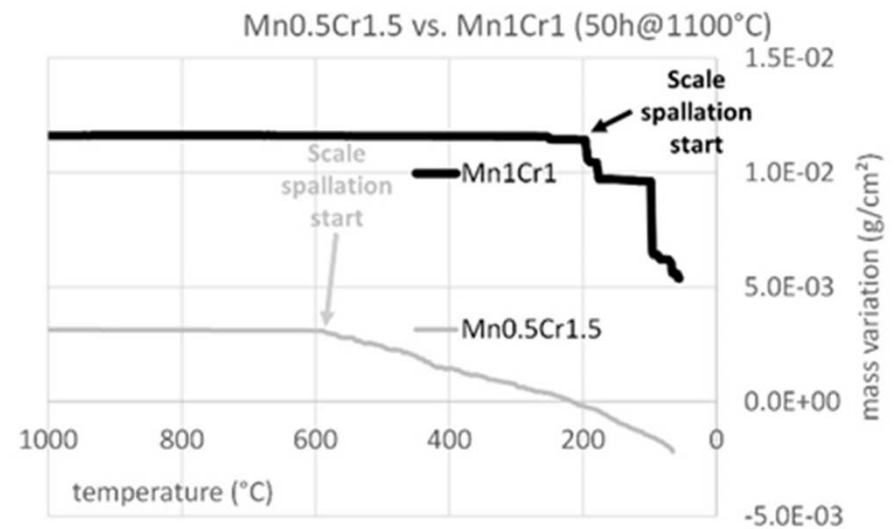
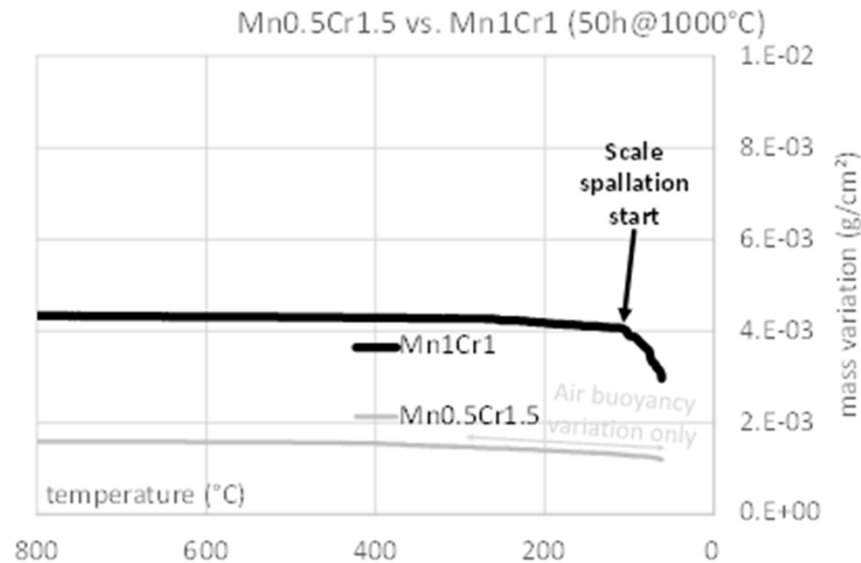


Cooling at -5 K min^{-1} from 1100°C

- Reminder of the mass gain isothermally achieved:
 $\approx 3.1 \text{ mg / cm}^2$ for Mn0.5Cr1.5, 4.7 mg / cm^2 (+TaC), 6.4 mg / cm^2 (+HfC)
- Little oxide scale loss in all cases (+TaC: slightly better behavior?)

Oxide scale spallation behavior

Exploitation of the cooling parts of the thermogravimetry curves



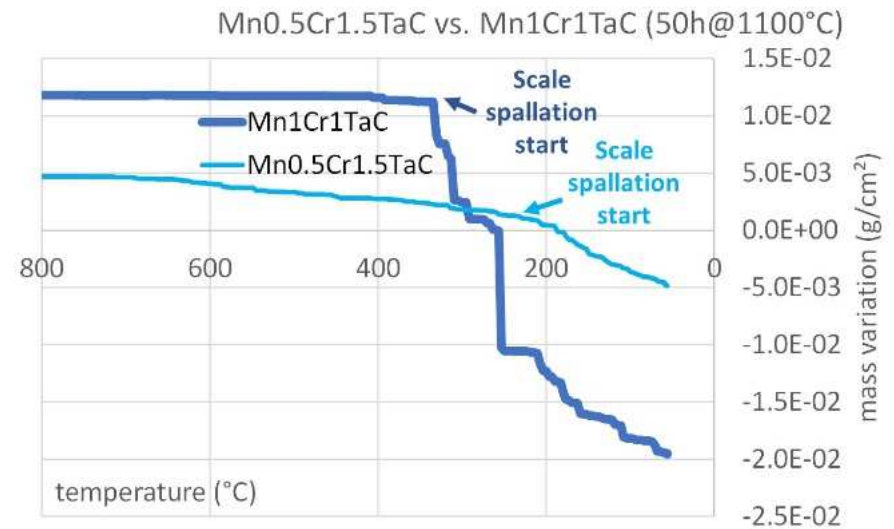
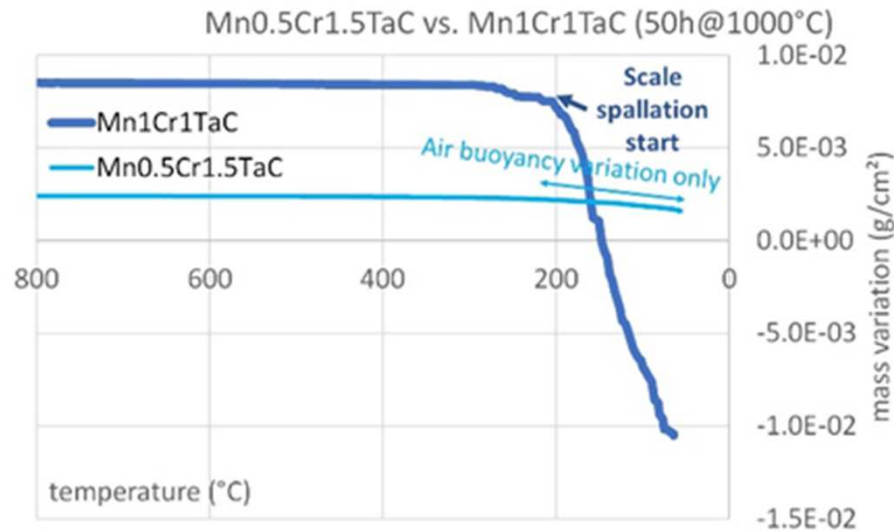
Mass variations for the carbide-free alloy (compared to the Mn1Cr1 alloys)

- From 1000°C: spallation only for the equimolar alloy
- From 1100°C: oxide scales spalled off for both alloys



Oxide scale spallation behavior

Exploitation of the cooling parts of the thermogravimetry curves

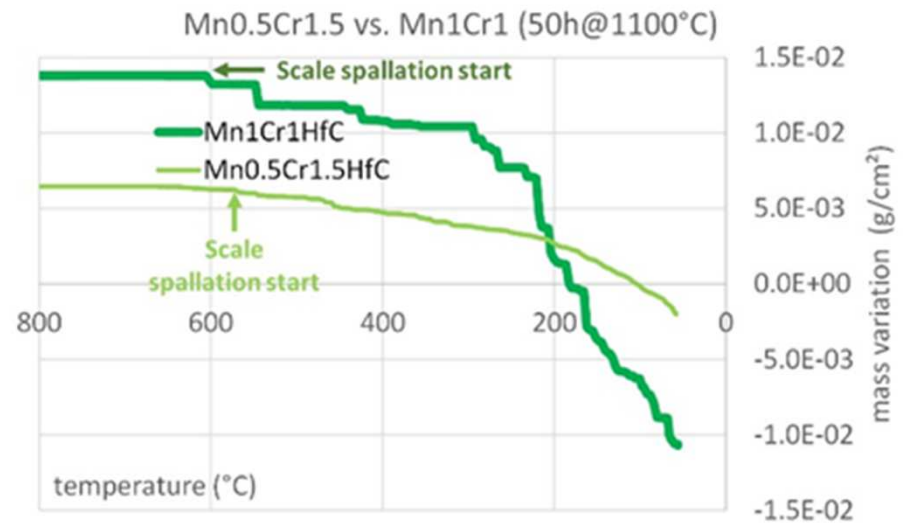
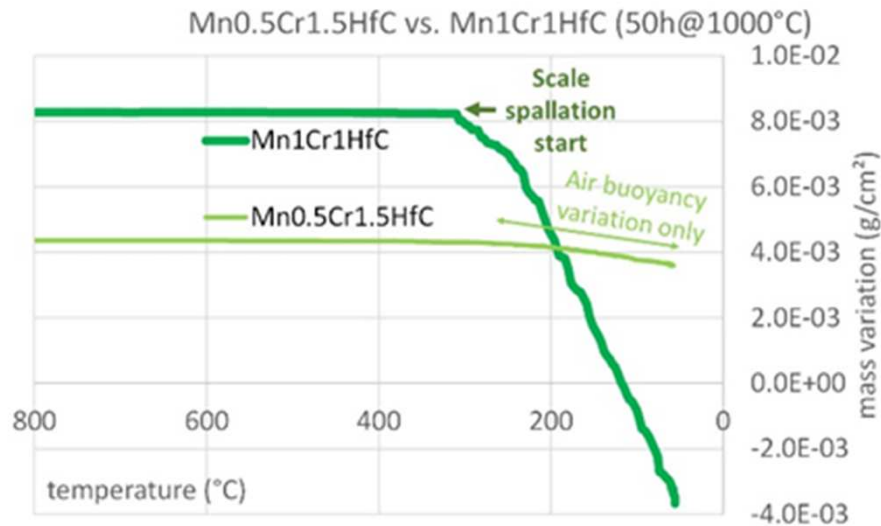


Mass variations for the TaC-containing alloy (compared to the Mn1Cr1TaC alloy)

- From 1000°C: spallation only for the Mn1Cr1TaC alloy
- From 1100°C: spallation in both cases, but much important for Mn1Cr1TaC

Oxide scale spallation behavior

Exploitation of the cooling parts of the thermogravimetry curves

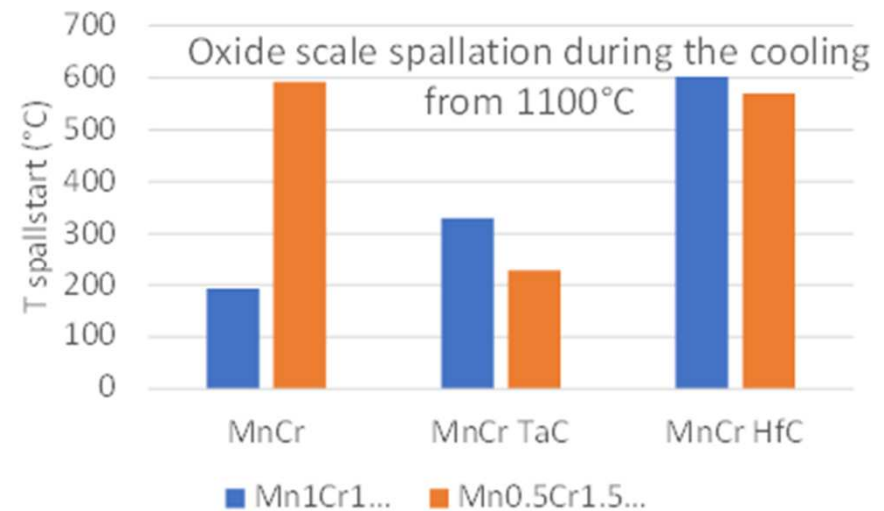
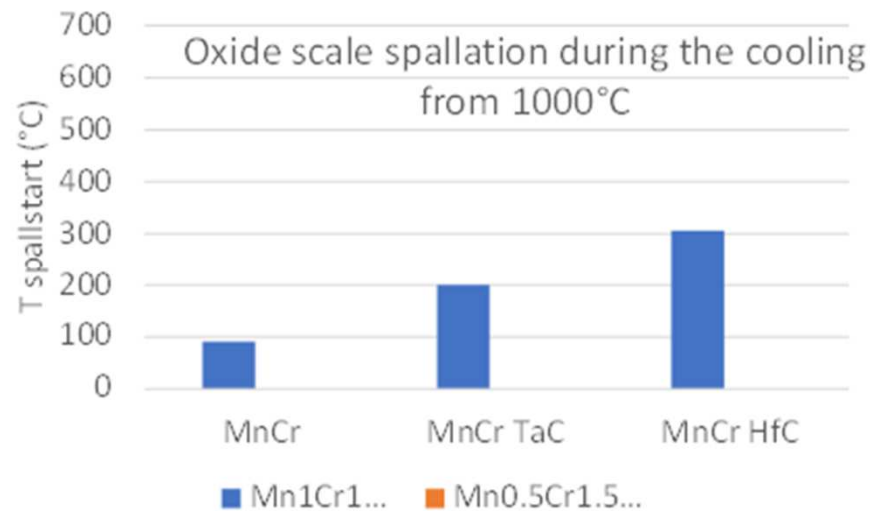


Mass variations for the HfC-containing alloy (compared to the Mn1Cr1HfC alloy)

- From 1000°C: (very important) spallation only for the Mn1Cr1HfC alloy
- From 1100°C: spallation in both cases, but much important for Mn1Cr1HfC

Oxide scale spallation behavior

Exploitation of the cooling parts of the thermogravimetry curves

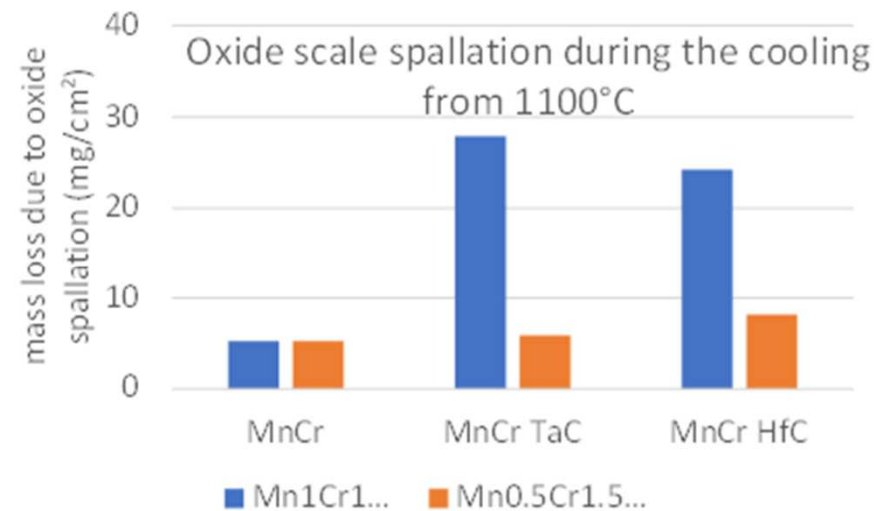
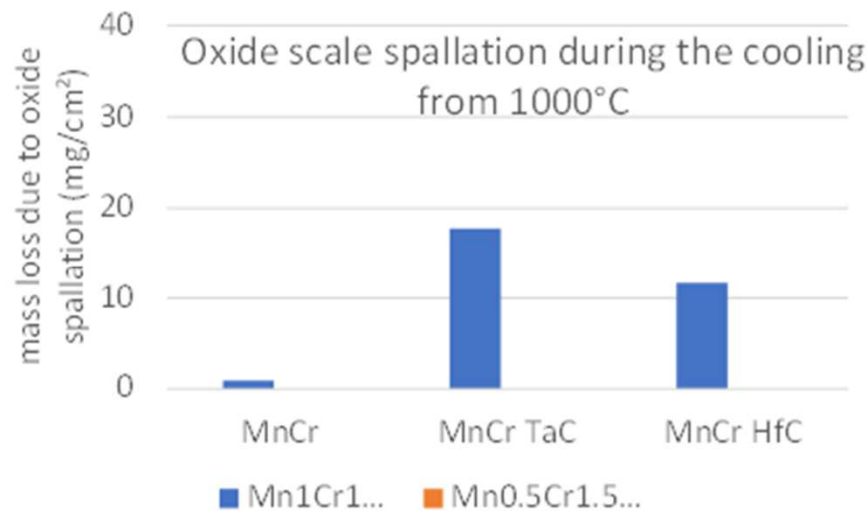


Two criteria for analyzing scale spallation: 1/temperature of spallation start

- For the Mn1Cr1 alloys spallation started sooner when carbides were present in alloy
- For the Mn1Cr1 alloys again, spallation started after a same decrease in temperature
- Very resistant against scale spallation after 50h at 1000°C the Mn0.5Cr1.5 alloys behave more or less as the Mn1Cr1 alloys after 50h at 1100°C

Oxide scale spallation behavior

Exploitation of the cooling parts of the thermogravimetry curves



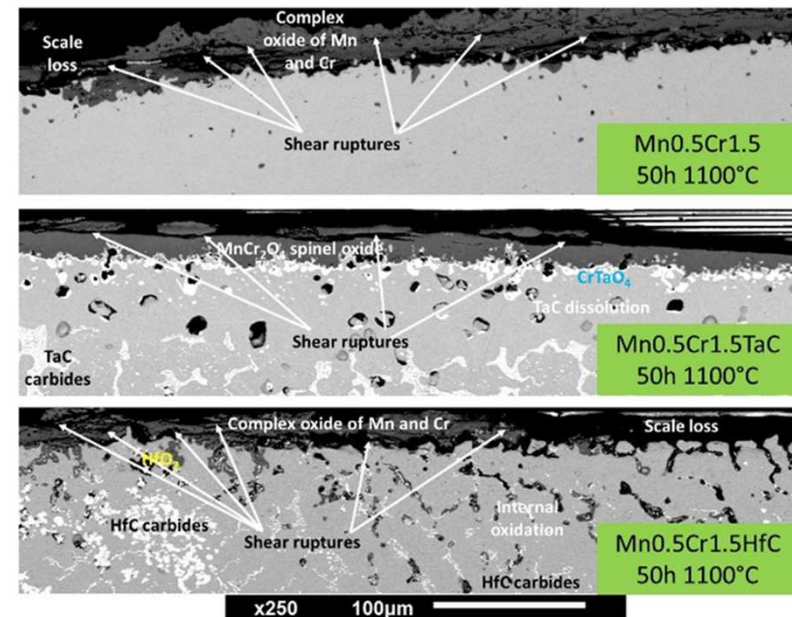
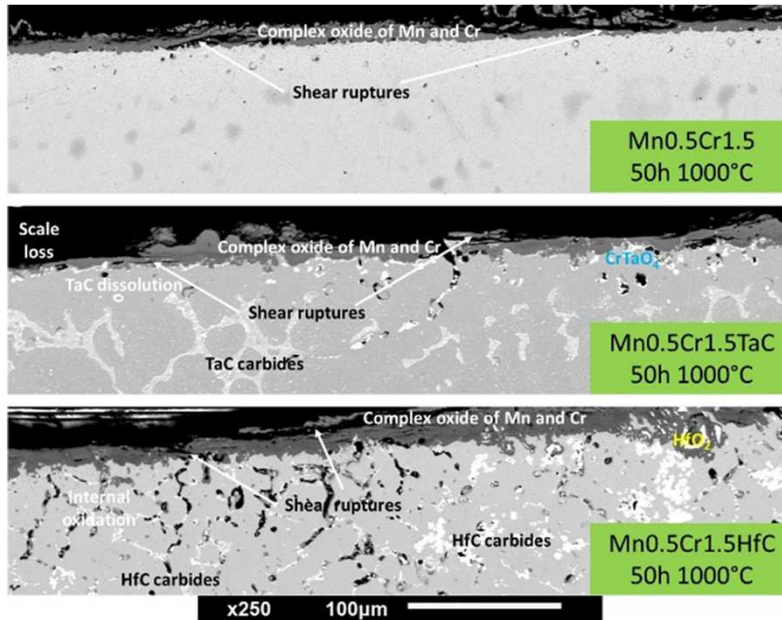
Two criteria for analyzing scale spallation: 2/total mass loss during cooling

- For all alloys mass loss is more important for cooling from 1100°C than from 1000°C
- For the Mn1Cr1 alloys much more mass was lost when carbides were present in alloy



Oxide scale spallation behavior

Cross-sectional observations where oxides were still here



- Many shear rupture of the scales at cooling (*and maybe also by handling even done carefully*)
- Disappearance of TaC in a depth increasing with temperature for a given duration
- Internal oxidation of HfC more extended inwards for 1100°C than for 1000°C

Conclusions / Outlooks

- ↓ Mn and ↑ Cr indisputably improve the resistance against scale spallation
 - Difference probably due to scales not as thick as for Mn1Cr1 alloys
 - But obvious lack of mechanical resistance of these multi-constituted scales
 - Mn: ↑ isothermal oxidation, takes part to scales more than Cr, thus a double deleterious effect on the scales which still exists even if %Mn is lowered
- Remove all Mn from Cantor's alloy derivatives destined to $T \geq 1000^{\circ}\text{C}$
- Testing new alloys as here and also for much faster and repeated coolings





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(corresponding TMS2024 proceeding: pp. 1194–1204)