

Isothermal High Temperature Oxidation of Cantor's-based MC-reinforced HEAs versus their Mn and Cr Contents

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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 & Interfaces: Chemical Reactivity of Materials” research group

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Outlines

- **Introduction**
- **Casting of the MC-containing HEA-based alloys**
- **Chemical compositions and microstructures**
- **Behavior in isothermal oxidation at high temperature**
 - Mass gain kinetics (thermo-balance)
 - Oxidation products (metallography characterization)
- **Conclusions**
- **Outlooks**



Introduction

- **High Entropy Alloys / the equimolar CoNiFeMnCr composition (Cantor)**
- **Adding MC carbides → enhancement of the H.T. mechanical resistance**
- **Unfortunately: bad oxidation behavior at 1000°C and beyond**
 - Fast mass gains; Thick oxides scales after less than 100 hours
 - Only minor role of chromium; Oxide scales involving Mn more than Cr
- **Possible way for improving resistance against oxidation: ↓ Mn and ↑ Cr**
- **THIS WORK: investigation of H.T. oxidation of new alloys with less Mn and more Cr**



Casting of the MC-containing HEA-based alloys

- Previous chemical compositions:

- Co-Ni-Fe-Mn-Cr (20 at.% each)
- 0.25C-3.8Ta-CoNiFeMnCr (bal.)
- 0.25C-3.7Hf-CoNiFeMnCr (bal.)

→ “*equimolar-based alloys*”

- New chemical compositions:

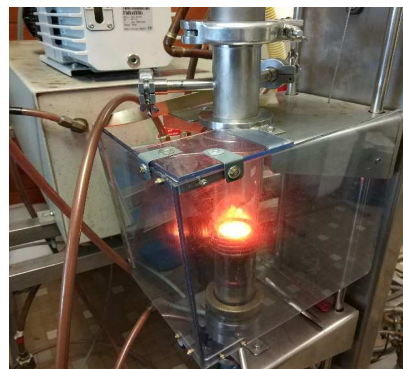
- 20 at.% Co – 20 at.% Ni – 20 at.% Fe –
~~20~~ **10 at.%Mn** – ~~20~~ **30at.%Cr**
- The same + 0.25 wt.%C-3.8 wt.%Ta
- The same + 0.25 wt.%C-3.7 wt.% Hf

→ “*modified alloys*”



Casting of the MC-containing HEA-based alloys

- 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

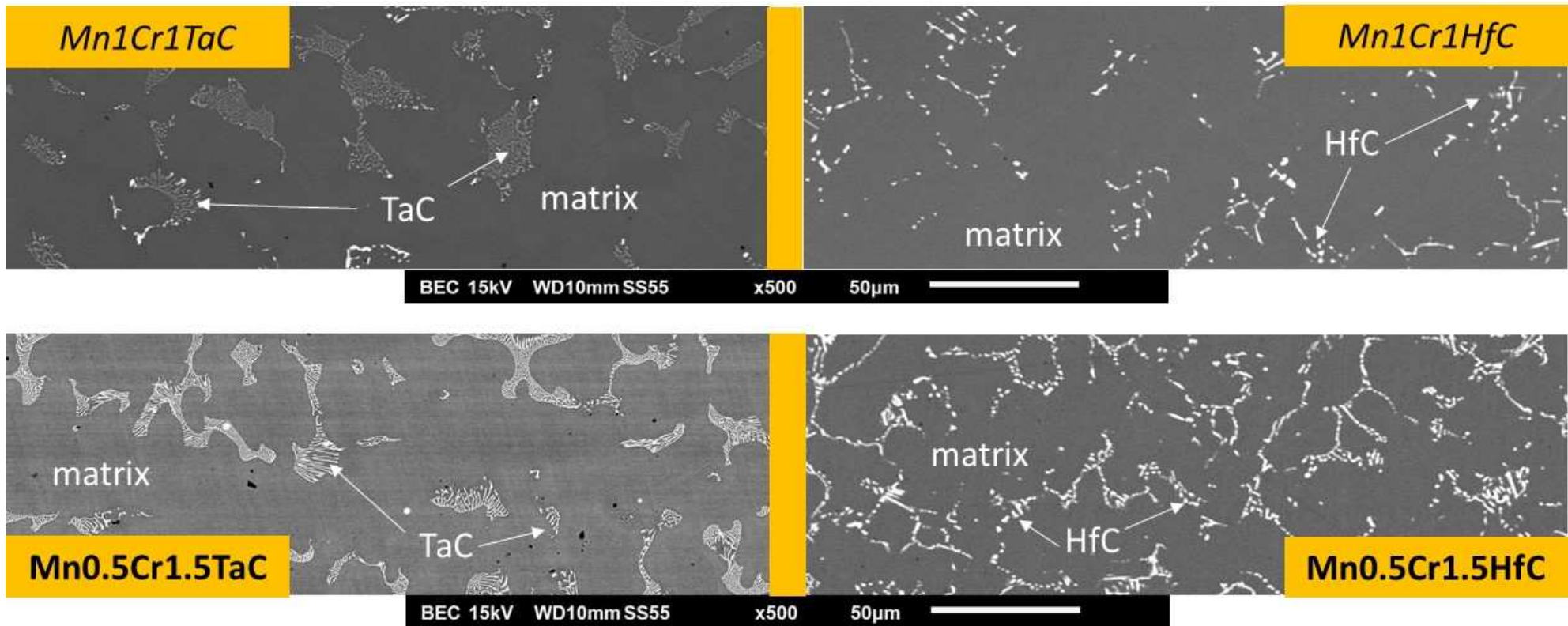


Obtained chemical compositions

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



Obtained microstructures (MC-containing only)



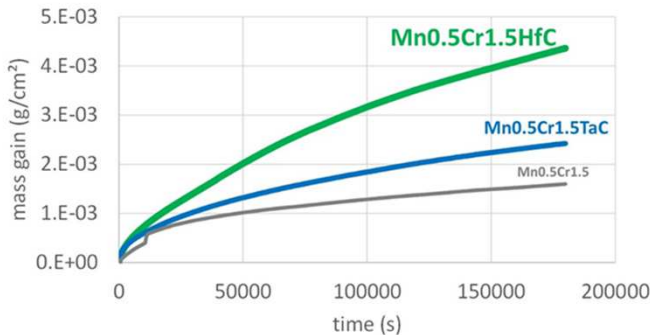
- Dendritic matrix and eutectic carbides (HfC: also some pre-eutectic ones)
- No clear influence of the changes in Mn and Cr; a little more carbides?



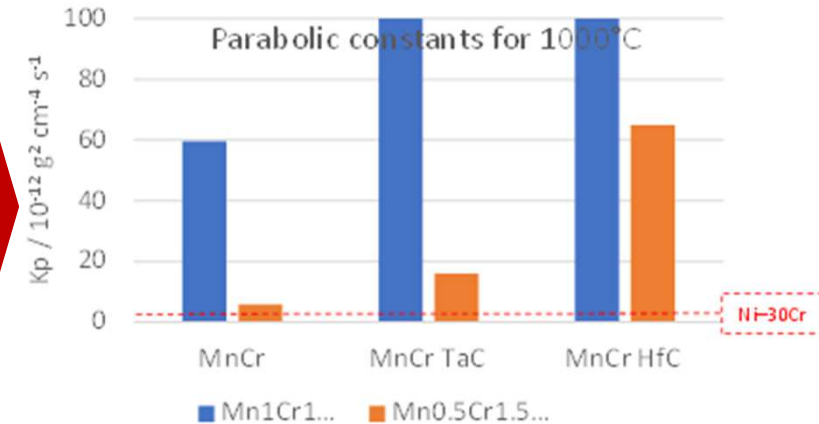
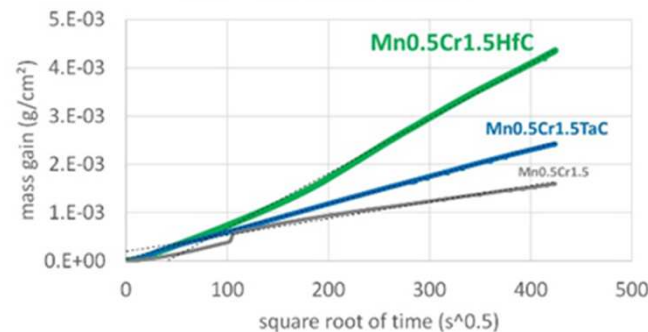
Behavior in isothermal oxidation at 1000°C

Mass gain kinetics

Oxidation of the CoNiFeMn_{0.5}Cr_{1.5}, " + TaC and " +HfC alloys at 1000°C



Oxidation of the CoNiFeMn_{0.5}Cr_{1.5}, " + TaC and " +HfC alloys at 1000°C



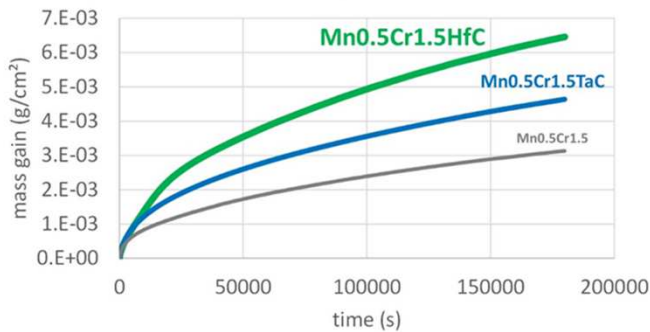
- Kinetics: globally parabolic
- Plot vs. square root of time: no linear loss, a little part of linear mass gain?
- Mn0.5Cr1.5 alloys: much more resistant than Mn1Cr1 alloys
- Mn0.5Cr1.5 simple or with TaC: worse than (but not far from) Ni-30Cr



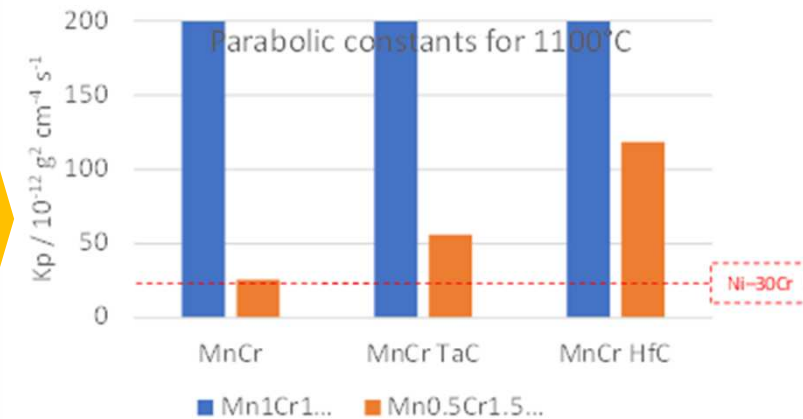
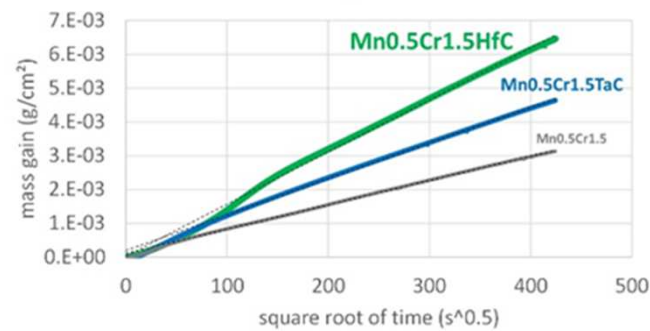
Behavior in isothermal oxidation at 1100°C

Mass gain kinetics

Oxidation of the CoNiFeMn_{0.5}Cr_{1.5} + TaC and +HfC alloys at 1100°C



Oxidation of the CoNiFeMn_{0.5}Cr_{1.5} + TaC and +HfC alloys at 1100°C

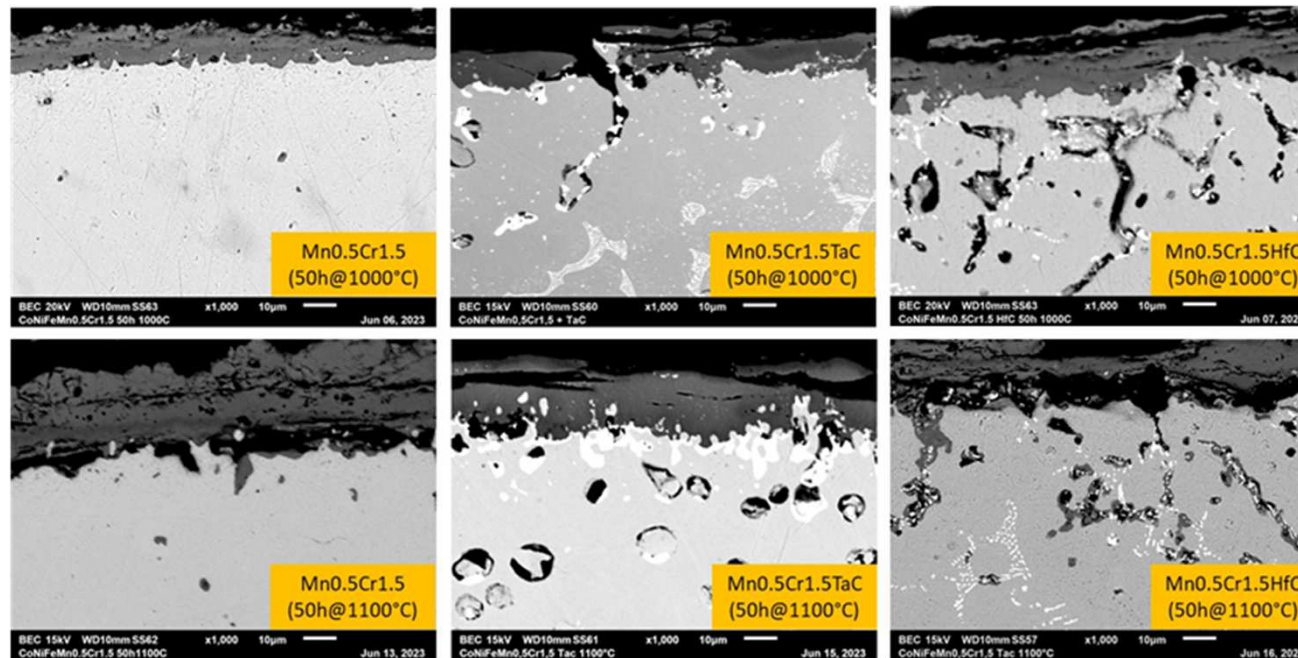


- Kinetics: parabolic
- Plot vs. square root of time: linear
- Again: Mn0.5Cr1.5 alloys: much more resistant than Mn1Cr1 alloys
- Again: Mn0.5Cr1.5 simple or with TaC: worse than (but not far from) Ni-30Cr



Behavior in isothermal oxidation at H.T.

Oxidation products: SEM/BSE imaging

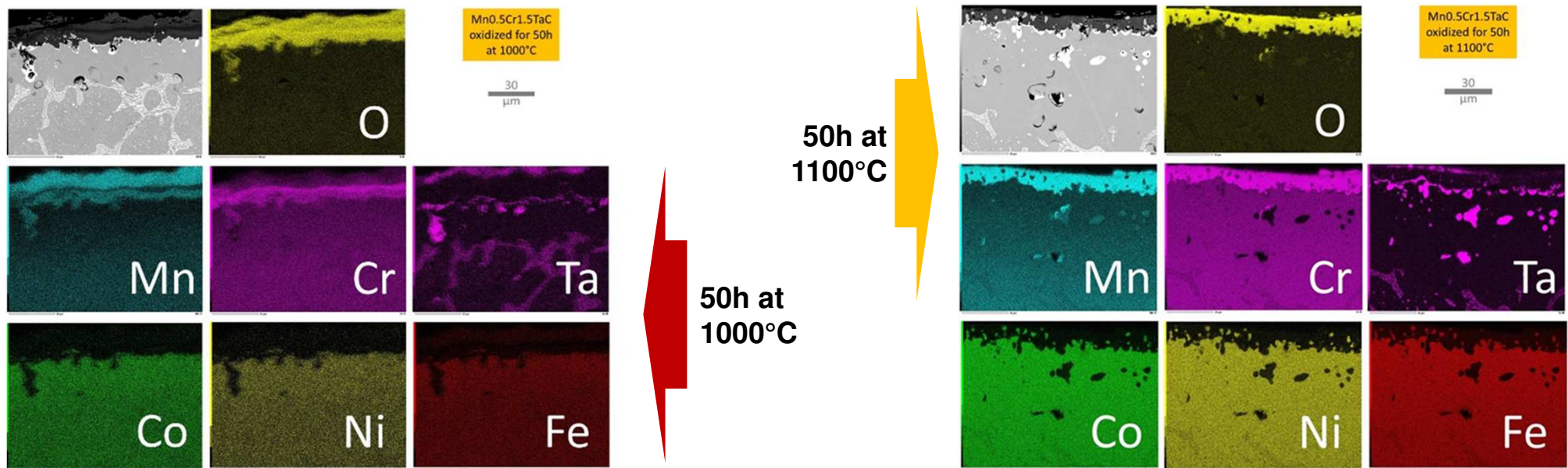


- Continuous oxide scales covering the alloys; multi-constituted; ± porous
- MC-containing alloys: TaC dissolution close to front, internal oxidation of HfC



Behavior in isothermal oxidation at H.T.

Oxidation products: elemental maps (example of the Mn_{0.5}Cr_{1.5}TaC alloy)

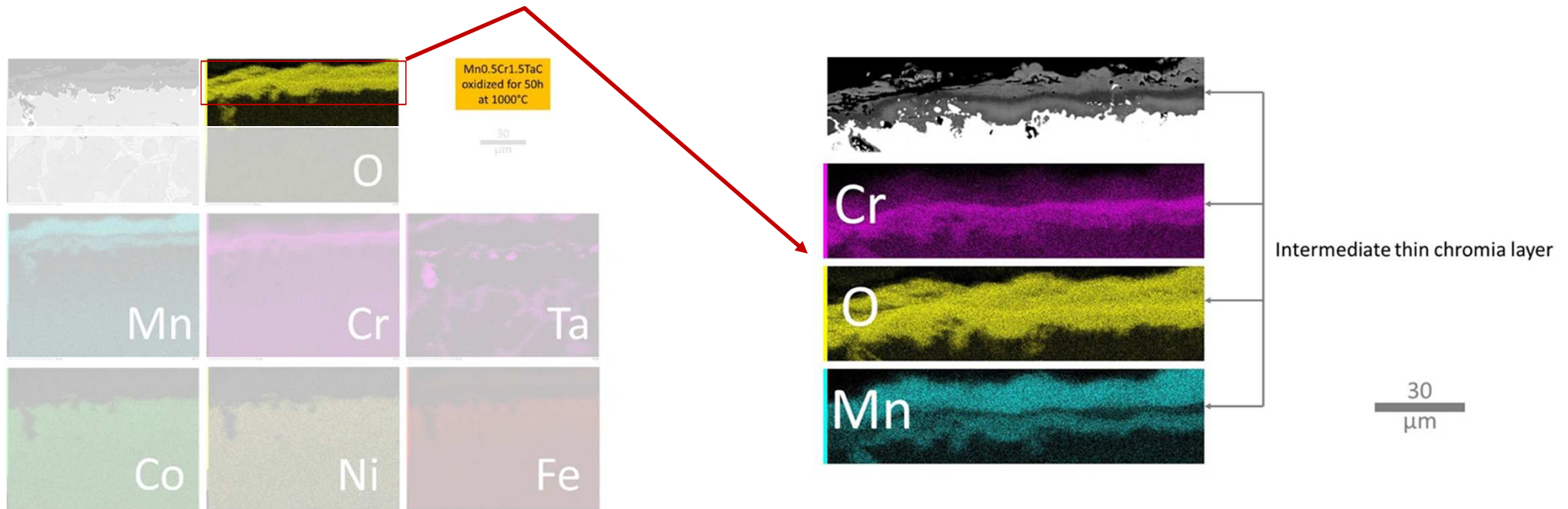


- Outward diffusion of Mn and Cr to be oxidized; no participation of Co, Ni, Fe
- Outward diffusion of Ta to be oxidized at the interface; HfC oxidized *in situ*



Behavior in isothermal oxidation at H.T.

Oxidation products: elemental maps (example of the Mn0.5Cr1.5TaC alloy)



- In some cases: formation of an internal continuous Cr₂O₃ scale
- Internal chromia scale: continuous but very thin; nevertheless an efficient contribution to the protection brought by the whole scale?

Behavior in isothermal oxidation at H.T.

Oxidation products: EDS spot analyses

Alloys ↓	Oxides at 1000°C (50h)	Oxides at 1100°C (50h)
Mn1Cr1	(Mn,Cr) ₃ O ₄ and/or (Mn,Cr) ₂ O ₃ MO, Cr ₂ O ₃	(Mn,Cr) ₂ O ₃ Cr ₂ O ₃
Mn0.5Cr1.5	(Mn,Cr)₂O₃ / Cr₂O₃ / MnCr₂O₄	(Mn,Cr)₂O₃ / Cr₂O₃ / MnCr₂O₄
Mn1Cr1TaC	(Mn,Cr) ₃ O ₄ and/or (Mn,Cr) ₂ O ₃ MO, Cr ₂ O ₃ , CrTaO ₄	(Mn,Cr) ₂ O ₃ Cr ₂ O ₃ , CrTaO ₄
Mn0.5Cr1.5TaC	(Mn,Cr)₂O₃ / Cr₂O₃ / MnCr₂O₄ / CrTaO₄	(Mn,Cr)₂O₃ / Cr₂O₃ / MnCr₂O₄ / CrTaO₄
Mn1Cr1HfC	(Mn,Cr) ₃ O ₄ and/or (Mn,Cr) ₂ O ₃ MO, Cr ₂ O ₃ , HfO ₂	(Mn,Cr) ₂ O ₃ Cr ₂ O ₃ , HfO ₂
Mn0.5Cr1.5HfC	(Mn,Cr)₂O₃ / Cr₂O₃ / MnCr₂O₄ / HfO₂	(Mn,Cr)₂O₃ / Cr₂O₃ / MnCr₂O₄ / HfO₂

- Mn still more involved in the oxide scales than Cr; Co, Ni, Fe: no role
- Outward diffusion of Ta to be oxidized; HfC oxidized *in situ*



Conclusions / Outlooks

- ↓ Mn and ↑ Cr indisputably improve the H.T. oxidation behavior
- The new oxidation resistances are still below the Ni–30Cr's one
- MC carbides degrade oxidation resistance (especially HfC)
- Oxides scales are multi-constituted and too porous to be really protective

→ Removing all Mn and testing CoNiFeCr + MC alloys

(alloys at the frontier between Cantor's alloy and Co-based/Ni-based alloys)

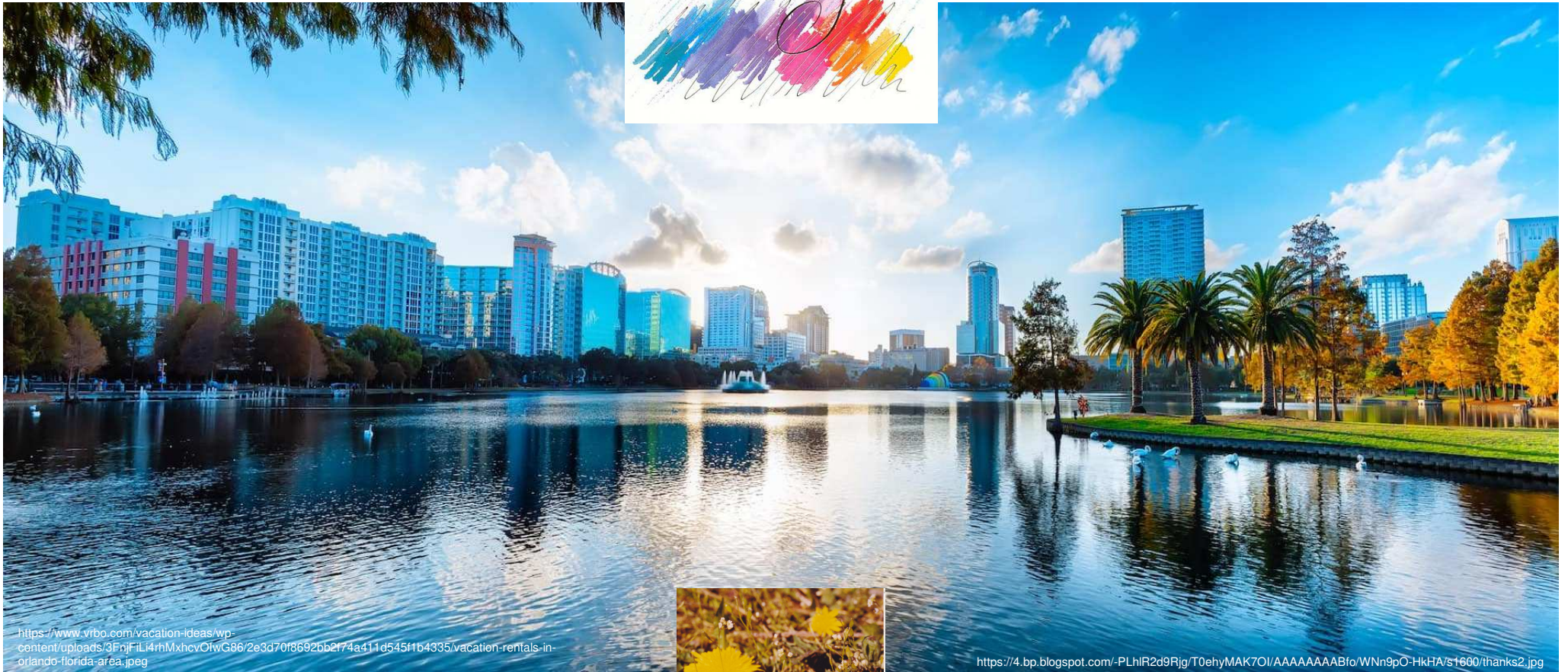
or

→ Replacing Mn by M' and testing CoNiFeM'Cr + MC alloys

(e.g. starting from the already existing CoNiFeCuCr HEAs)



Thank You!



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(corresponding TMS2024 proceeding: pp. 1262–1272)

