

HIGH TEMPERATURE OXIDATION OF CoNiFeMnCr HIGH ENTROPY ALLOYS REINFORCED BY MC-CARBIDES

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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., HDR Chemistry**
- **Foundry, metallurgy, corrosion, microstructures and properties of superalloys at high temperature**

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

Work achieved without funding sources

No conflict of interest

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Outlines

- Introduction
- Examples of cast high creep-resistant Co-based superalloys with MC
- Elaboration of MC-strengthened HEA-based superalloys by foundry
- Obtained as-cast microstructures and microstructure behaviors at H.T.
- Some examples of creep tests results at HT
- Behavior in oxidation at high temperature
 - Tests in furnace / metallographic characterization
 - On going tests in thermo-balance for kinetic results
- Conclusions
- Outlooks

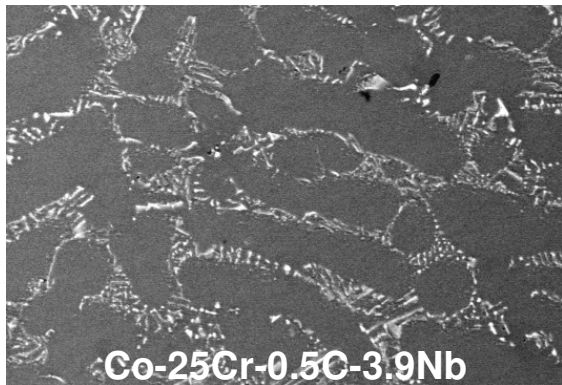


Introduction

- **High Entropy Alloys: a recently developed family of metallic alloys with high intrinsic strength**
- **One of the earliest HEAs: the equimolar CoNiFeMnCr (Cantor)**
- **Polycrystalline equi-axed versions: weakness in grain boundaries (GB)**
- **Reinforcement of GB?**
 - Favoring dendritic microstructures
 - Promoting the formation of hard particles in GB and in the interdendritic spaces
- **A solution: introducing C and Ta or Hf to produce refractory and stable script-like eutectic MC carbides (as is some Co-based superalloys)**

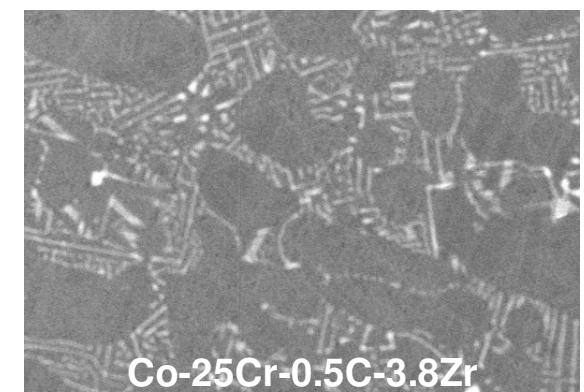
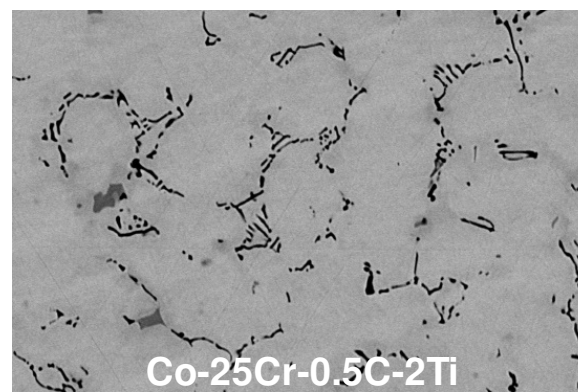
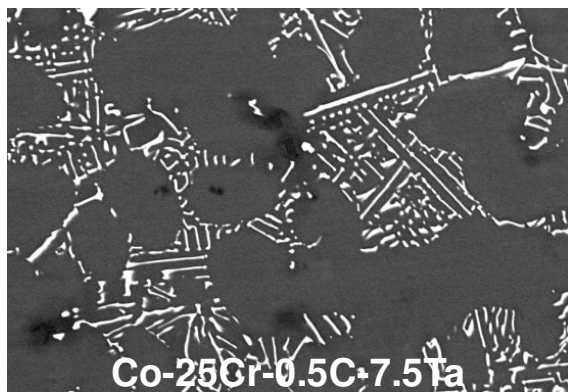
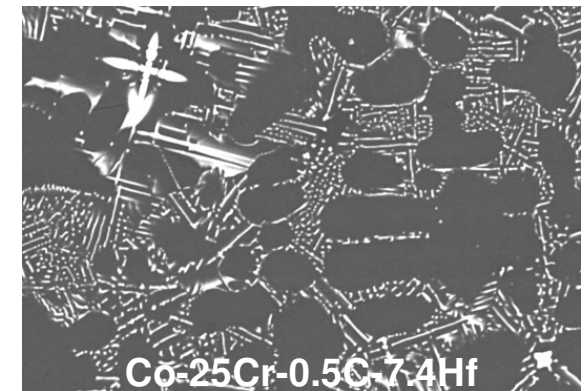


Examples of MC-strengthened Co-b^d model alloys



Model alloys

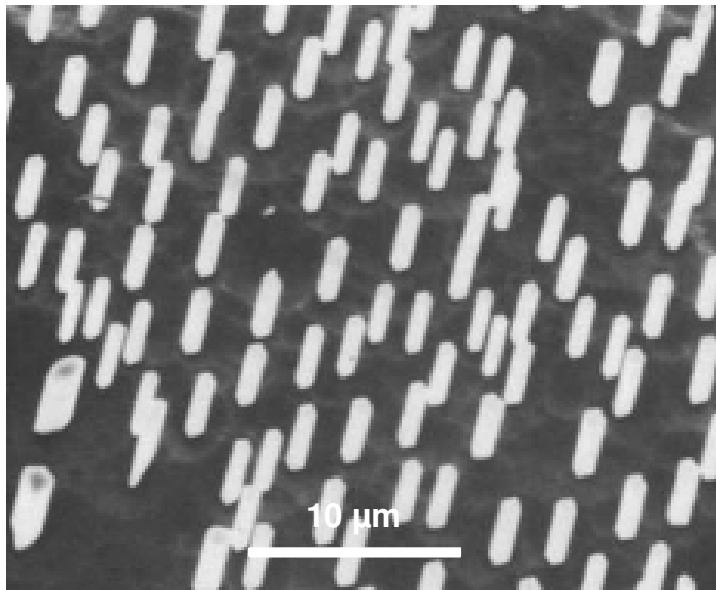
25 μ m



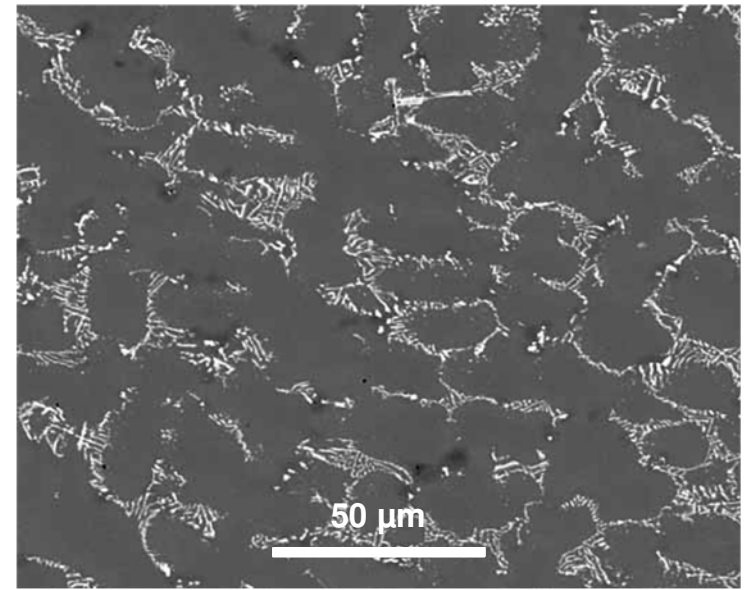
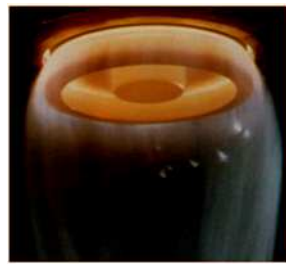
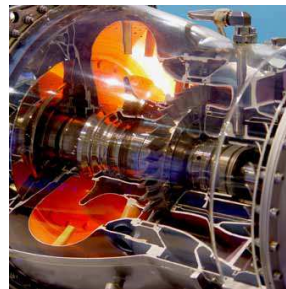
Journal of Alloys and Compounds (2009) 481 pp.746–754.
Journal of Metallic Material Research (2019) 2(01) pp.10–18.

Examples of MC-strengthened Co superalloys

Pre-industrial and industrial alloys for turbine blades, glass-shaping tools...



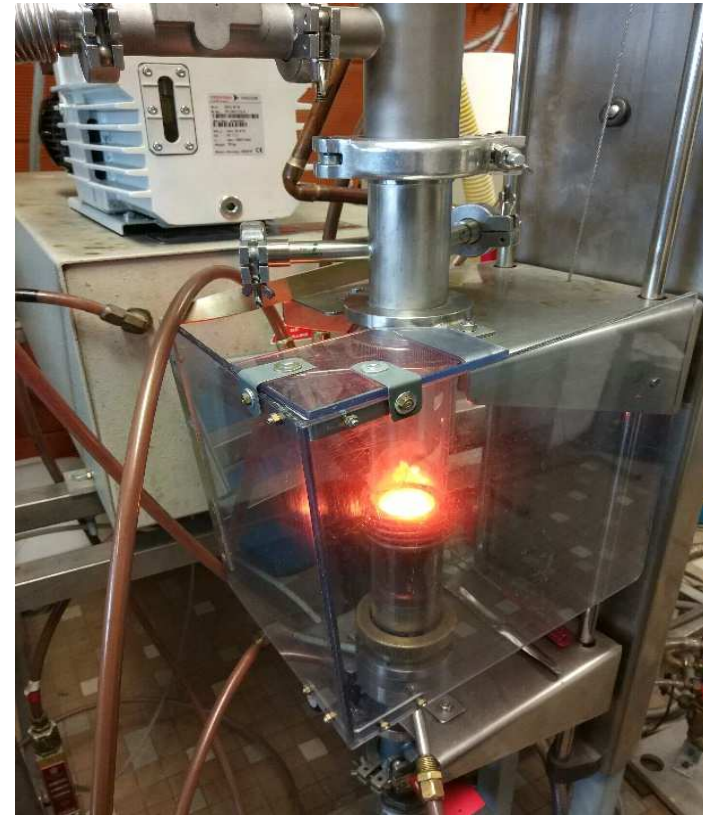
Materials Science and Engineering (1987) 88 pp.253–260.



La Revue de Métallurgie (2004) 101(9) pp.651–662.

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 ($\approx 1700^{\circ}\text{C}$)**



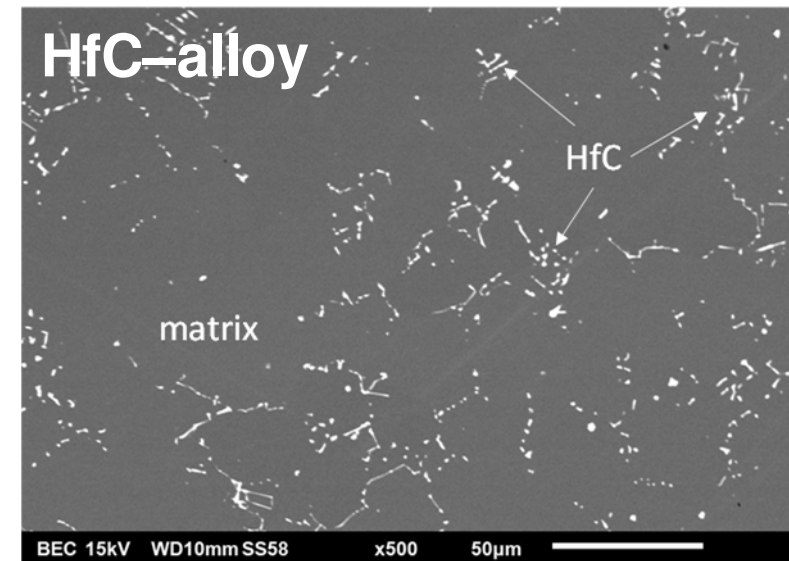
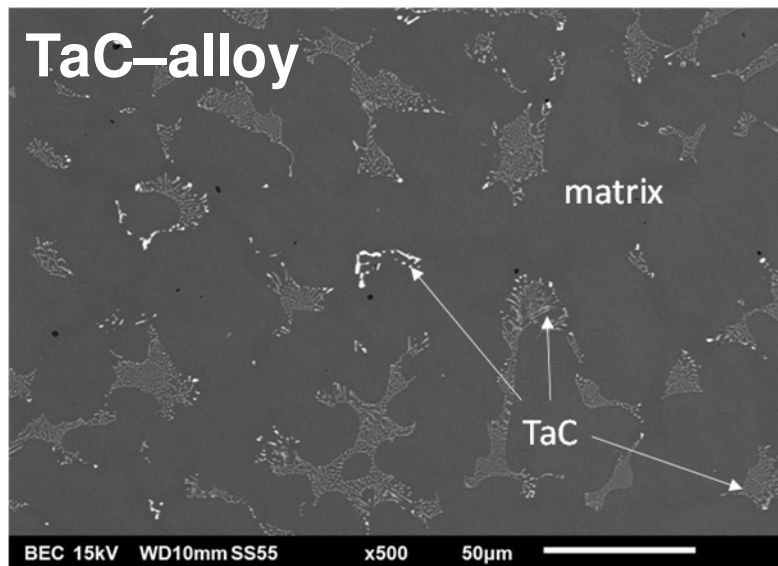
Chemical compositions of the MC–HEAs

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

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



As-cast microstructures of the MC-HEAs

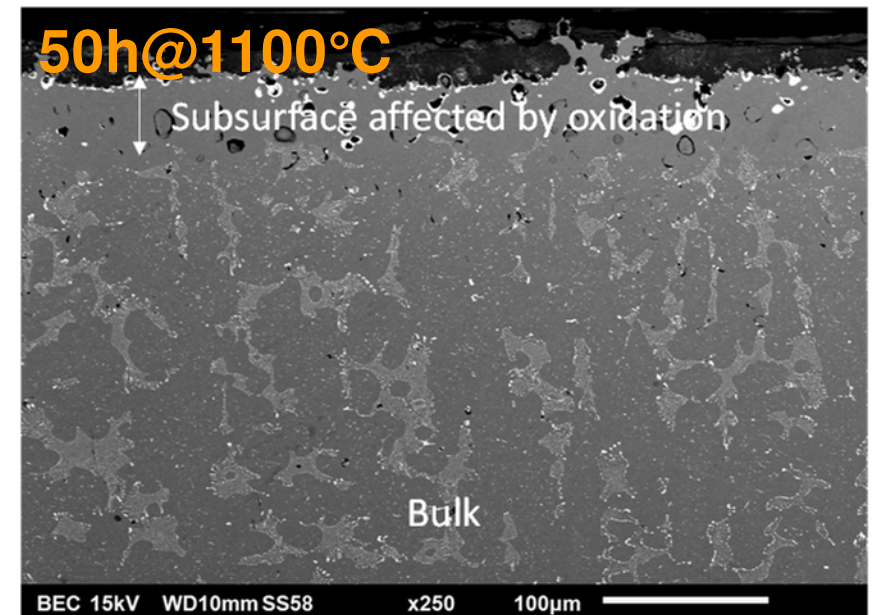
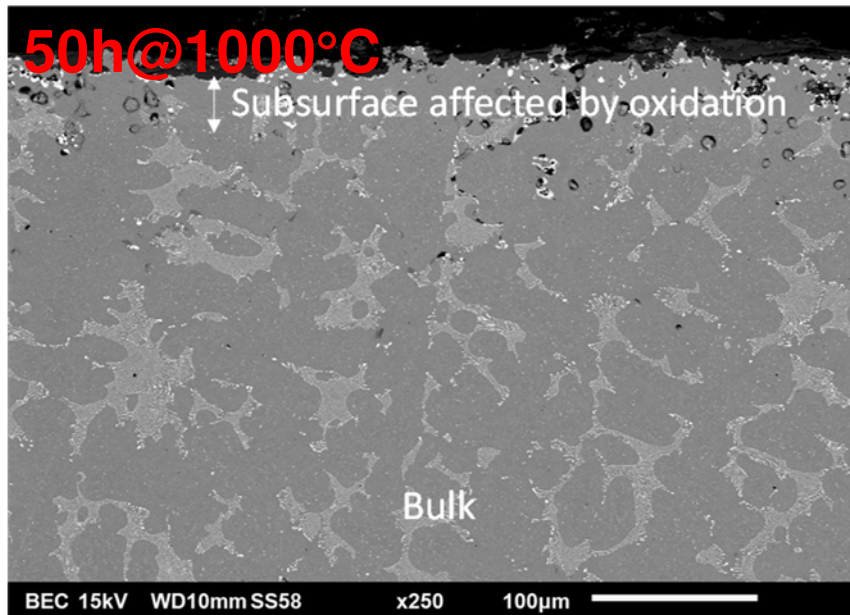


Matrix (homogeneous in Co, Ni, Fe, Mn and Cr, & ≈ 2 wt.%Ta or ≈ 0 wt.%Hf)
Script-like MC carbides (as in the previously shown Co-based alloys)

Journal of Metallic Material Research (2022) 5(2) pp.1–10.

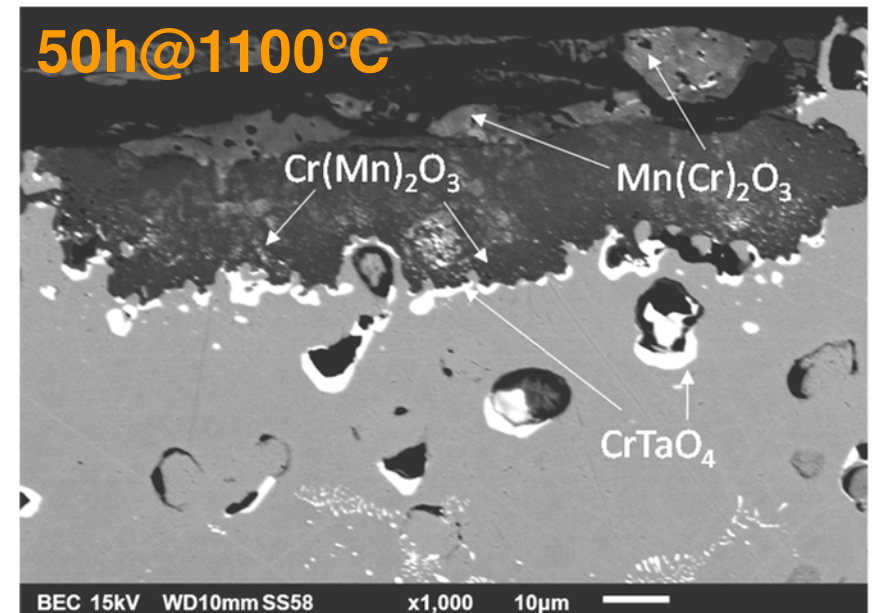
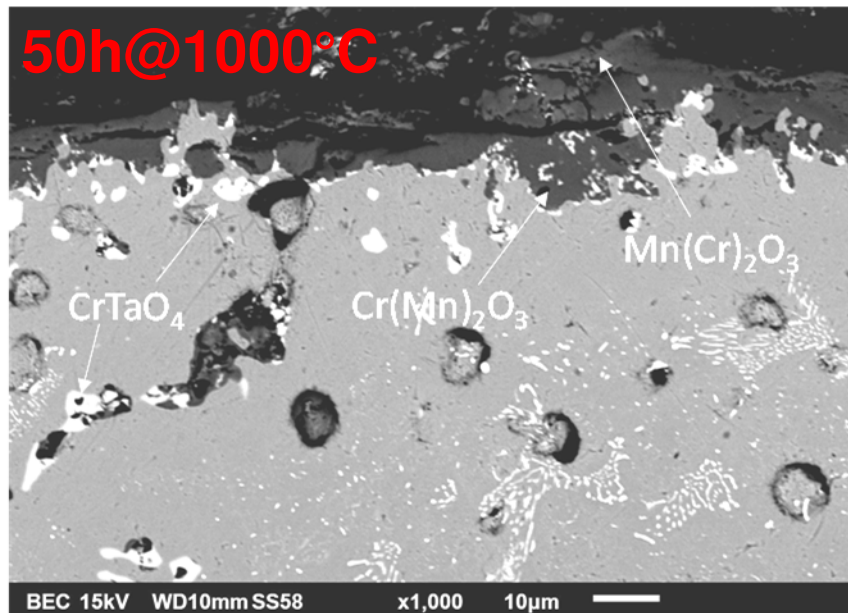
Journal of Engineering Sciences and Innovation (2022) 7(3) pp.305–314.

Oxidation of the TaC–alloy at H.T.



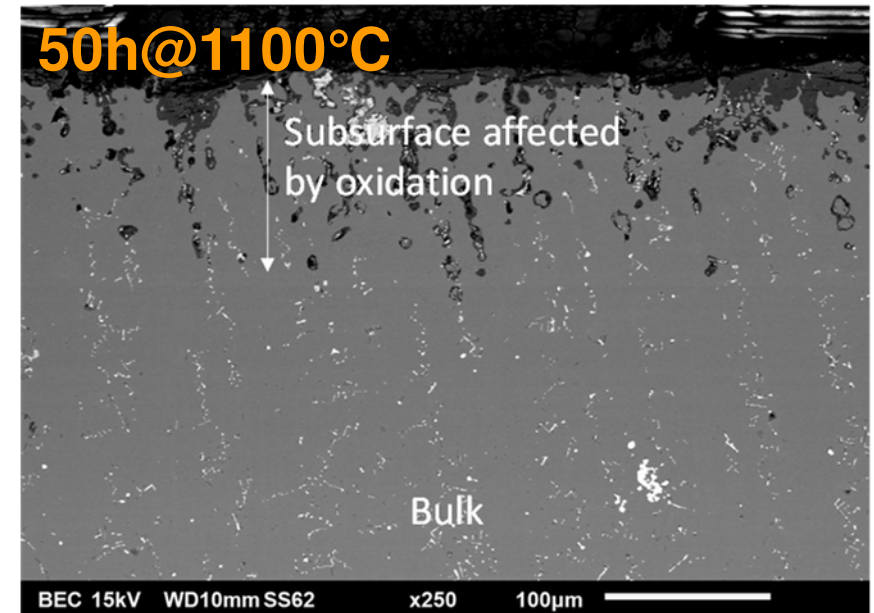
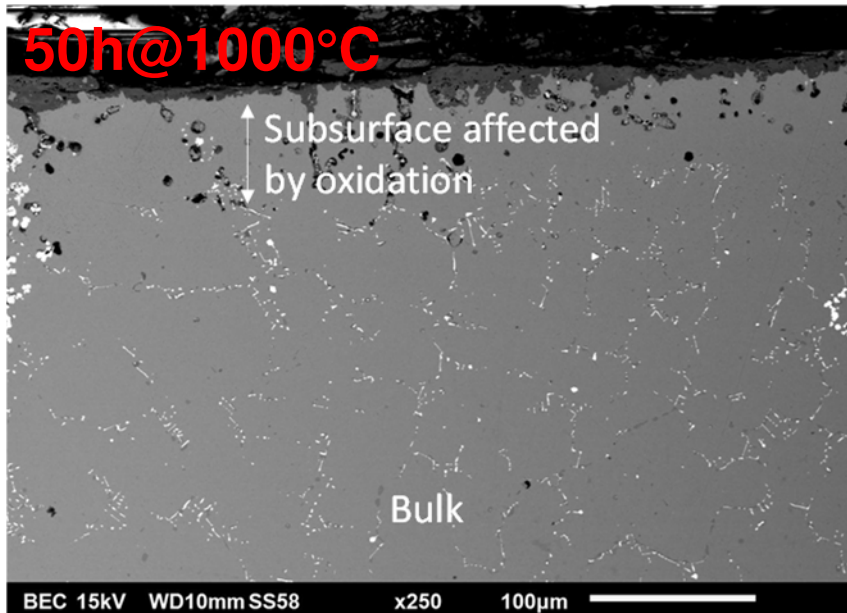
Severe oxide spallation during cooling
Subsurface deterioration (internal oxides, TaC disappearance) deeper if temperature higher

Oxides formed in the case of the TaC–alloy



(Mn,Cr)₂O₃ oxides with various values of the Mn/Cr ratio; CrTaO₄ at the oxide scale/ alloy interface
Morphology evolution of the TaC (fragmentation, coalescence); secondary TaC precipitation at 1000°C

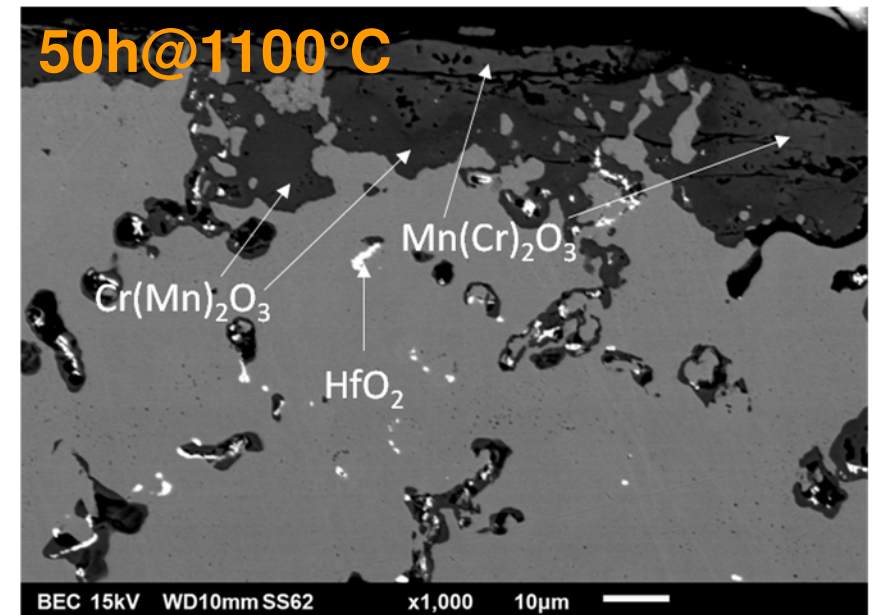
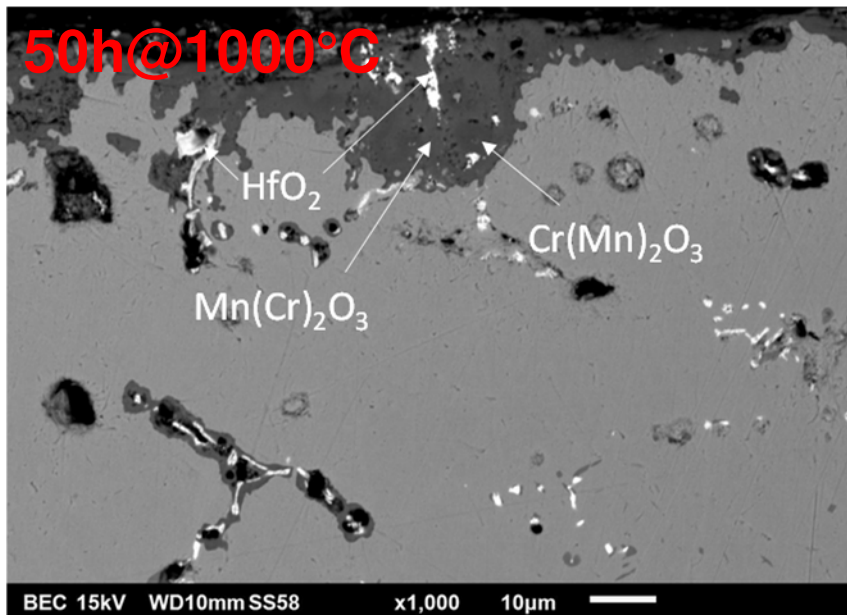
Oxidation of the **HfC**-alloy at H.T.



Severe oxide spallation during cooling

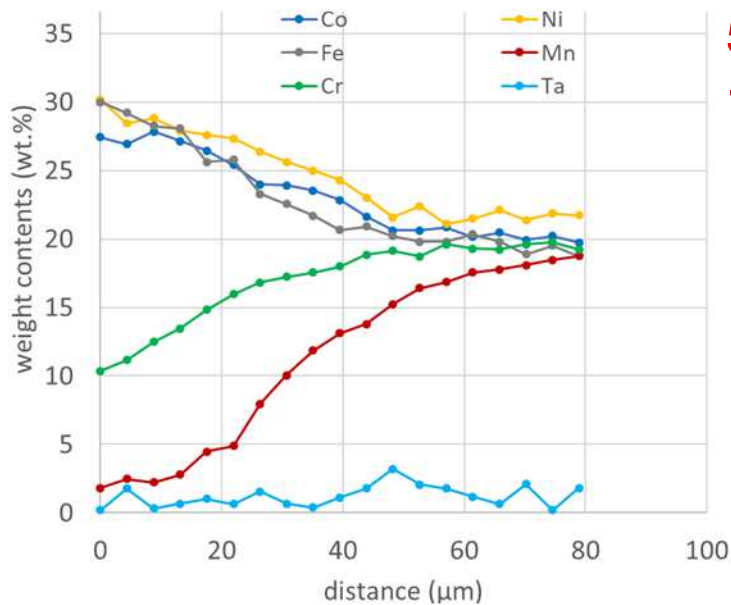
Subsurf. deterioration (int. oxides, HfC disappear.) deeper than for the TaC-alloy, deeper for higher T

Oxides formed in the case of the **HfC**-alloy



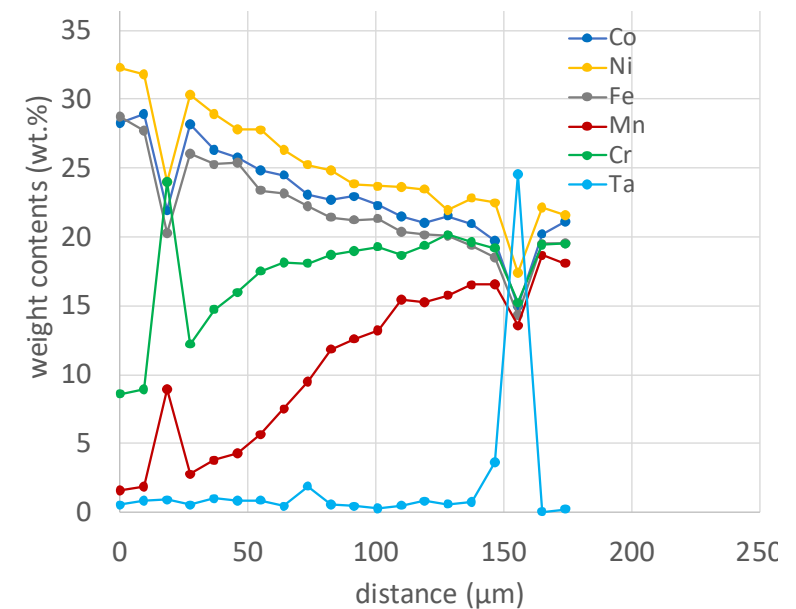
(Mn,Cr)₂O₃ oxides with various values of the Mn/Cr ratio; Cr₂O₃ at the interface separating oxide scale and alloy; internal oxidation (HfO₂)

Chemical changes in subsurface for TaC–alloy



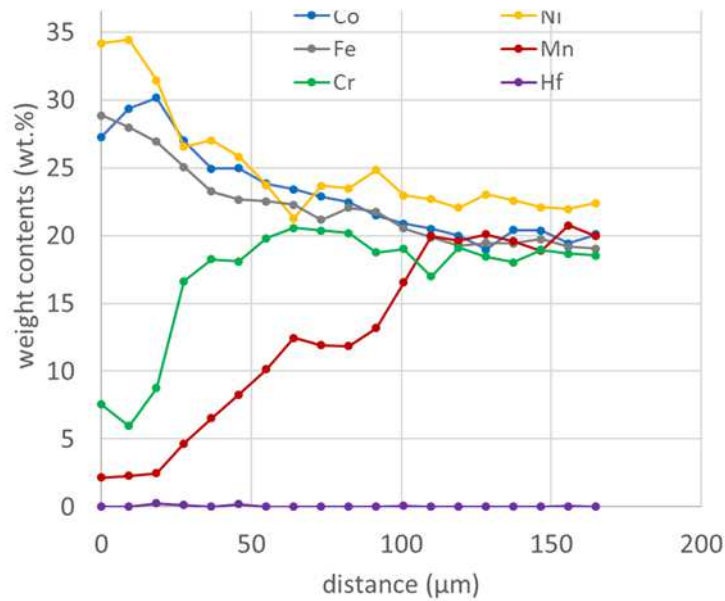
50h@
1000°C

50h@
1100°C



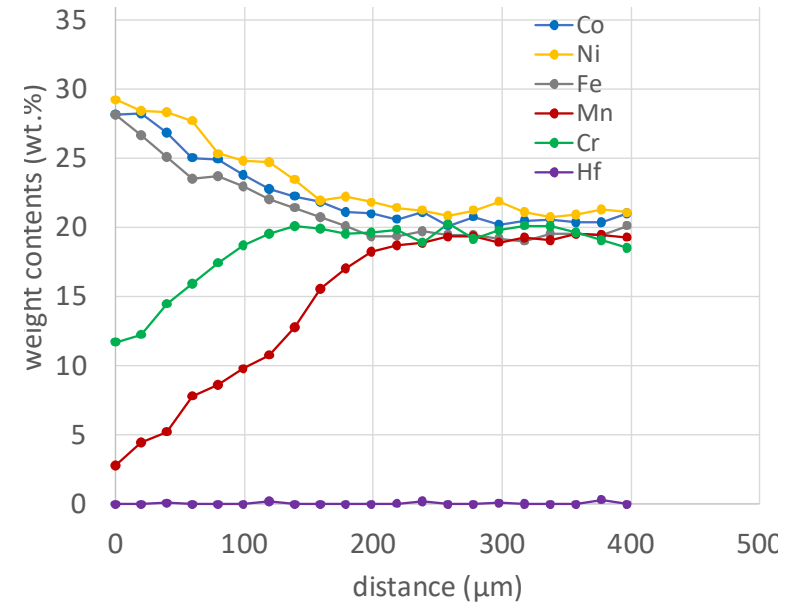
**Mn and Cr were the only species to diffuse toward the oxidation front (Mn more than Cr)
The alloy lost more Mn than Cr; the depths depleted in Mn and in Cr increase with T**

Chemical changes in subsurface for HfC–alloy



50h@
1000°C

50h@
1100°C



Here too, Mn and Cr were the only species to diffuse toward the oxidation front (Mn more than Cr), the alloy lost more Mn than Cr, and the depths depleted in Mn and in Cr increase with T



Quantification attempt

- **Balance sheets in X = Mn and Cr:** $\frac{m_X}{S} = \rho_{alloy} \times \int_0^{D_{dept} h_X} [f_w^X - f_w^X(x)] \times dx$
 - TaC-alloy: loss of 9 (resp. 17) mg/cm² of Mn+Cr at 1000°C (resp. 1100°C)
 - HfC-alloy: loss of 12 (resp. 18) mg/cm² of Mn+Cr at 1000°C (resp. 1100°C)

(Cantor: 6 (resp. 17) mg/cm² of Mn+Cr at 1000°C (resp. 1100°C))

- **Corresponding M₂O₃ thicknesses:** $e_{(Mn,Cr)_2O_3} = \frac{n_{(Mn,Cr)_2O_3} \times (2 \times (M_{Cr} + M_{Mn}) / 2 + 3 \times M_O)}{S \rho_{(Mn,Cr)_2O_3}}$
 - TaC-alloy: 20 (resp. 50) μm at 1000°C (resp. 1100°C)
 - HfC-alloy: 35 (resp. 54) μm at 1000°C (resp. 1100°C)

(Cantor: 19 (resp. 52) mg/cm² of Mn+Cr at 1000°C (resp. 1100°C))



Quantification attempt

- **Corresponding Kp values:**
 - **TaC-alloy: 24 (resp. 160) $\times 10^{-12}$ g² cm⁻⁴ s⁻¹ at 1000°C (resp. 1100°C)**
 - **HfC-alloy: 75 (resp. 180) $\times 10^{-12}$ g² cm⁻⁴ s⁻¹ at 1000°C (resp. 1100°C)**

$$Kp = \frac{1}{2} \times \frac{\left(\frac{3}{2} \times \left(\frac{n_{Cr}}{S} + \frac{n_{Mn}}{S}\right) \times M_O\right)^2}{Timox}$$

Journal of Chemical Engineering Research Updates (2022) 9 pp.60–71.

For comparison:

Cantor: 18 (resp. 162) $\times 10^{-12}$ g² cm⁻⁴ s⁻¹ at 1000°C (resp. 1100°C) / same procedure;

Ni-30Cr alloy: 3 (resp. 23 $\times 10^{-12}$ g² cm⁻⁴ s⁻¹) at 1000°C (resp. 1100°C) / thermogravimetry

(*Oxidation of Metals* (2005) 64(3/4) pp. 235–252.



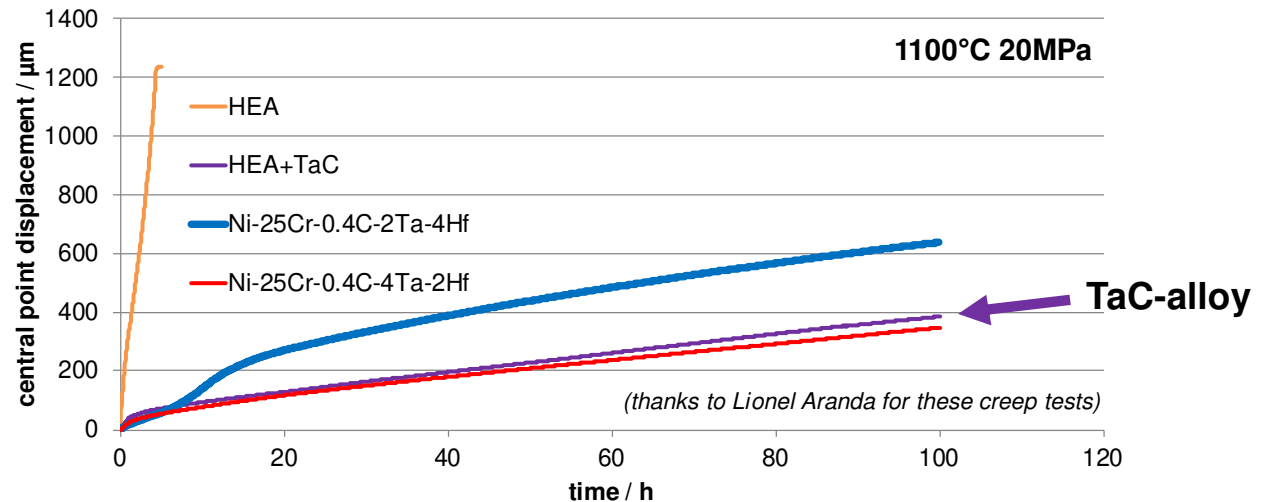
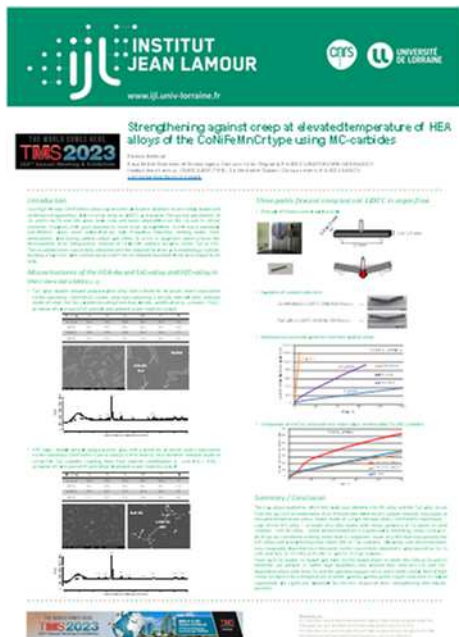
Conclusions

- **Successful change of a Co(Cr) matrix by a CoNiFeMnCr one without change in dendrites and script–like eutectic MC carbides**
- **Instead Cr for the Co(Cr)+MC superalloys, this is now Mn which plays the main role in H.T. oxidation**
- **Protective Cr_2O_3 is for a great part replaced by $(\text{Mn,Cr})_2\text{O}_3$, less protective, and also more threatened by oxide spallation**
- **The presence of MC tends to degrade the H.T. oxidation behavior of the Cantor's alloy (particularly true for HfC)**
- **The three alloys of this work are all much less resistant than a really chromia–forming alloy (as Ni–30Cr)**



Outlooks

To take benefit from the interesting creep resistance of these MC–strengthened HEAs...



Poster presented here (TMS2023) “Strengthening Against Creep at Elevated Temperature of HEA Alloys of the CoNiFeMnCr Type Using MC-Carbides” & Supplemental proceeding: pp.1103–1111.



Outlooks

... it is compulsory to significantly improve the H.T. oxidation behavior of these alloys; this can be made, for instance, by:

- Increasing their Cr contents (i.e. CoNiFeMnCr_{1.5} + TaC or HfC),**
- Adding Al in the list of the present elements**
- Applying a protective coating (i.e. PVD Cr pack–cementation)**

In parallel, thermogravimetry runs are currently in progress for a better knowledge of the oxidation kinetics.





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Fabrication, Structures and Properties of High Entropy Alloys and Refractory High Entropy Alloys

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