



**HAL**  
open science

## **Metallographic follow-up of the oxidation progress with time of cast Cantor alloy at 1000°C**

Lyna Amrouche, Romin Chevalme, Siouare Hammi, Yasmina El Hadad, Erwan Etienne, Patrice Berthod

### **► To cite this version:**

Lyna Amrouche, Romin Chevalme, Siouare Hammi, Yasmina El Hadad, Erwan Etienne, et al.. Metallographic follow-up of the oxidation progress with time of cast Cantor alloy at 1000°C. TMS2025 154th Annual Meeting & Exhibition, Mar 2025, Las Vegas (Nevada ), United States. <hal-05012805>

**HAL Id: hal-05012805**

**<https://hal.science/hal-05012805v1>**

Submitted on 31 Mar 2025

**HAL** is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.



Distributed under a Creative Commons CC BY-NC-ND 4.0 - Attribution - Non-commercial use - No Derivative Works - International License

C-4



## Metallographic follow-up of the oxidation progress with time of cast Cantor alloy at 1000°C

Lyna Amrouche<sup>1</sup>, Romin Chevalme<sup>1</sup>, Siouare Hammi<sup>1</sup>, Yasmina El Hadad<sup>1</sup>, Erwan Etienne<sup>2</sup>, Patrice Berthod<sup>1,2</sup>  
<sup>1</sup>Faculté des Sciences et Technologies, Campus Victor Grignard, F-54500 VANOEUVRE-LES-NANCY (France)  
<sup>2</sup>Institut Jean Lamour, CNRS (UMR 7198), 2 allée André Guinier, Campus Artem, F-54000 NANCY (France)  
[patrice.berthod@univ-lorraine.fr](mailto:patrice.berthod@univ-lorraine.fr)

### Introduction

The high entropy alloys (HEAs) of the Cantor's type (equimolar CoNiFeMnCr) contain less Co and Ni than superalloys and are thus less dependent on these critical elements. Their refractoriness and intrinsic strength over a large range of temperatures let think that they are possibly able to play the role of basis for new alloys for applications at moderate – and maybe – to high temperatures. Unfortunately, due to the significant presence of manganese associated to a rather low chromium content, these alloys oxidized rapidly in air when temperature is about 1000°C. This is problematic for the exploitation of versions reinforced by MC-carbides and able to resist creep at this level of temperature [1] but which present a similarly bad behavior in hot oxidation [2]. It was reported by numerous authors that, after oxidation at temperatures equal to 1000°C or below, the oxidation products formed upon the Cantor's alloys are composed of various types of oxides, mainly involving manganese and chromium simultaneously. Their protective effect is much less efficient than the chromia one. Seemingly the progress of development of these oxides is not well known at 1000°C. The present work is a tentative to better understand when and in which order these different oxides appear and evolve thereafter.

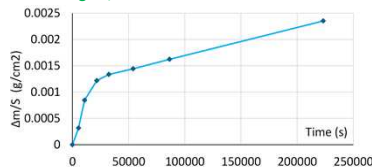
### Experimental details of the study

- Elaboration of a 40g–weighing ingot by high frequency induction melting (50kW CELES furnace, 100 kHz, several A, 5 kV max) in inert atmosphere
- Control of composition and microstructure by scanning electron microscopy (SEM, JEOL 6010LA) and energy dispersion spectrometry (EDS)
- Ingot cut to obtain parallelepipeds to grind with SiC papers (#1200–grit) for the oxidation tests
- Dimensions measurement with a caliper and weighing with a precision balance for each sample
- Introduction in a tubular resistive furnace (Carbolite) of a nacelle containing the sample (centered in the hottest zone).
- {1.5h, 3h, 6h, 9h, 15h, 24h or 62h}–exposure at 1000°C, ended by nacelle removing out of the furnace, natural cooling down to ambient temperature, second weighing of the oxidized samples
- Examination with the SEM in secondary electrons and back scattered electrons modes (SE and BSE, respectively) and characterization by EDS spot analysis and elemental mapping
- Embedding in a {resin + hardener} mixture rigidifying at ambient temperature, transversal cutting, grinding/polishing, cross-sectional SEM/BSE observation of the external and internal oxides, EDS spot analyses and elemental mapping carried out on oxides and in subsurface



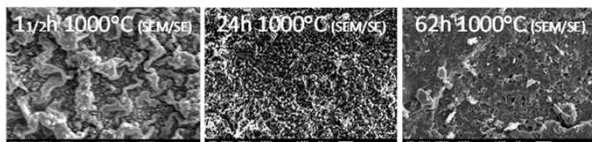
### Mass variation

- First, a linear mass gain (5 first hours)
- Later: parabolic / parilinear mass gain; no tentative to determine the value of a parabolic constant



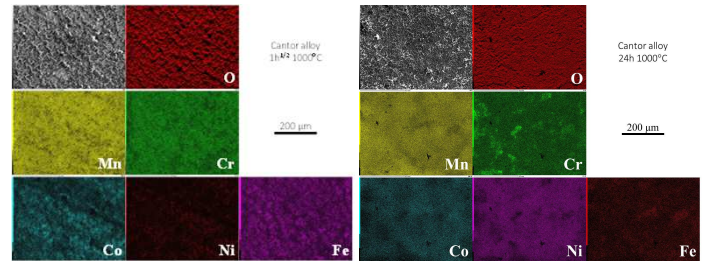
### Outermost aspect of the oxide scales

- Initially made of a mix of coarse oxides and much finer ones (1.5h to >6h)
- Later: evolution for finer structure (> 6h to < 24h)
- Between 24h and 62h: appearance here and there of some new coarse oxides
- No relevant results of spot or full frame analysis, except that Mn (major) and Cr (minor) → the most present metals in the outermost part of the scales



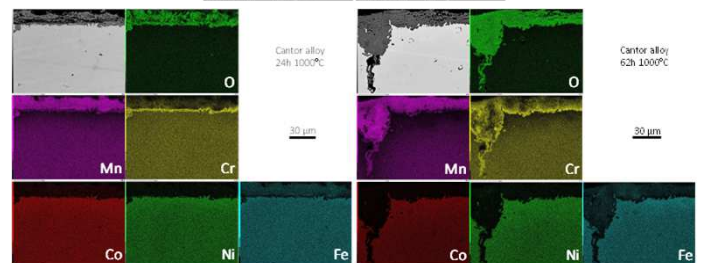
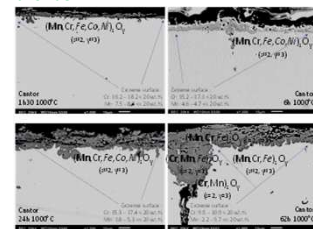
### Outermost aspect of the oxide scales

- EDS elemental mapping: maps not homogeneous, except for oxygen
- Regions locally richer in Co, Ni and Fe → poorer in Mn (e.g. 1.5h, 3h, 24h, 62h)
- Zones rich in Cr often also rich in Mn (e.g. 3h) or, in contrast, poor in Mn (9h, 15h)
- Some zones rich in Co and Fe, and poor in Ni and Cr (e.g. 15h)



### Cross-sectional observation and EDS analyses

- Average scale thickness ↑ with time (2μm for 1.5h → 20 μm for 62h) ≡ mass gain
- Internal oxidation development ↑ with time (probably along grain boundaries)
- Outermost scale: Mn more present than Cr, innermost scale: Cr more present than Mn
- Fe also always present in oxide whatever the location (except close to the alloy)
- Interface scale/alloy: chromia (involving or not a little part of Mn)
- Strong modification of composition in outermost alloy: Cr content progressively decreased from 20 wt.% (initial) to 10 wt.% (62h), Mn content decreased from 20 to 6 wt.% at least
- EDS elemental mapping: oxide scale principally involving Mn and Cr and chromium particularly present in innermost scale; already visible for 1.5h and still true for 62h
- EDS mapping: also evidences the progress of Mn and Cr impoverishments in subsurface; already visible for 1.5h Mn–depletion reaches 30μm for 62h; not visible before 6h, Cr–depletion reaches 15 μm for 62h of oxidation
- Mn appears as the main element to diffuse towards the oxidation front and to take part to the growth of the external oxide.



### Conclusion

- Earliest hours: all the five elements were involved by oxidation
- Several hours later: only Mn and Cr are still oxidizing and the subsurface is progressively impoverished mainly in Mn (more) and Cr (less)
- General oxidation of the alloy (thus involving also Co and Ni) is expected slightly later, when Mn and Cr no longer able to diffuse due to too important depletion depths (mainly Mn)

The corresponding supplemental proceeding TMS is available; see pp.962–971.

### References :

- [1] P. Berthod: Strengthening against creep at elevated temperature of HEA alloys of the CoNiFeMnCr type using MC-carbides. TMS 2023 152rd Annual Meeting & Exhibition Supplemental Proceedings 1103–1111.
- [2] P. Berthod: High temperature oxidation of CoNiFeMnCr high entropy alloys reinforced by MC-carbides. TMS 2023 152rd Annual Meeting & Exhibition Supplemental Proceedings 933–941.

