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ALTERNATIVE DISSOLUTION AND OXIDATION BEHAVIOR OF 316L(N) STEEL AT 550°C IN LIQUID SODIUM CONTAINING LOW CONCENTRATION OF OXYGEN

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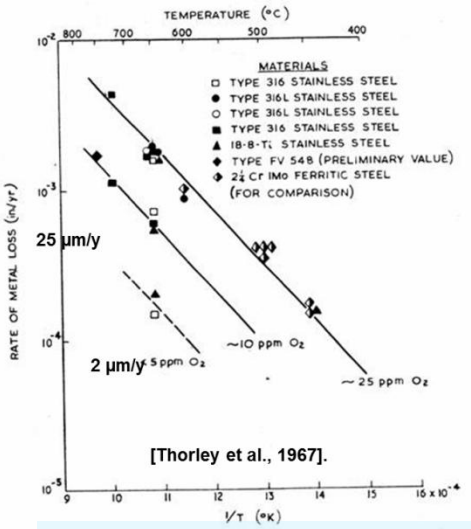
1) CONTEXT AND STATE OF THE ART

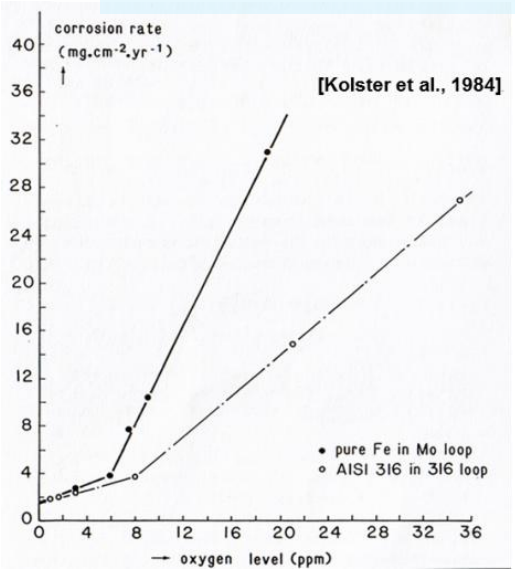
- **CONTEXT** : Generation IV - SFR - ASTRID
  - Corrosion data and prediction of service life-time of reference materials as 316L(N) - 60 y – through corrosion modeling

- **STATE OF THE ART :** large literature in relation to fast reactors applications
  - excellent corrosion resistance of steels at high T & high flow in pure liquid Na but the semi-empirical models (316L - 1y - T > 600°C) are not conservative
  - As stainless steels and refractory metals present low solubility's even at high temperature in pure liquid sodium
  - But impurities such as oxygen drastically increase the dissolution rates of stainless steels because of the formation of ternary oxides ($NaCrO_2$, Na_4FeO_3) that are relatively (?) soluble in liquid sodium
  - Oxygen role unclear (catalytic effect, complex formation)

- **Reactor**: Oxygen as low as possible to maintain corrosion low

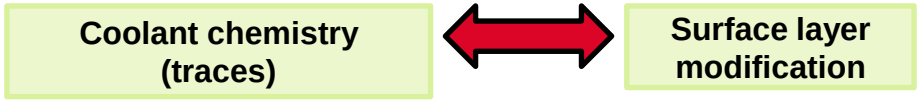


Dissolution and mass transfer



1) OBJECTIVE AND PLAN

- **OBJECTIVE :** validate the hypothesis that oxidation may occur during transient or alternate chemical conditions in heat transfer systems because of alternate conditions varying with coolant chemistry and materials surface layer evolutions with operating time in agreement with thermodynamic conditions, which is necessary for long term modeling

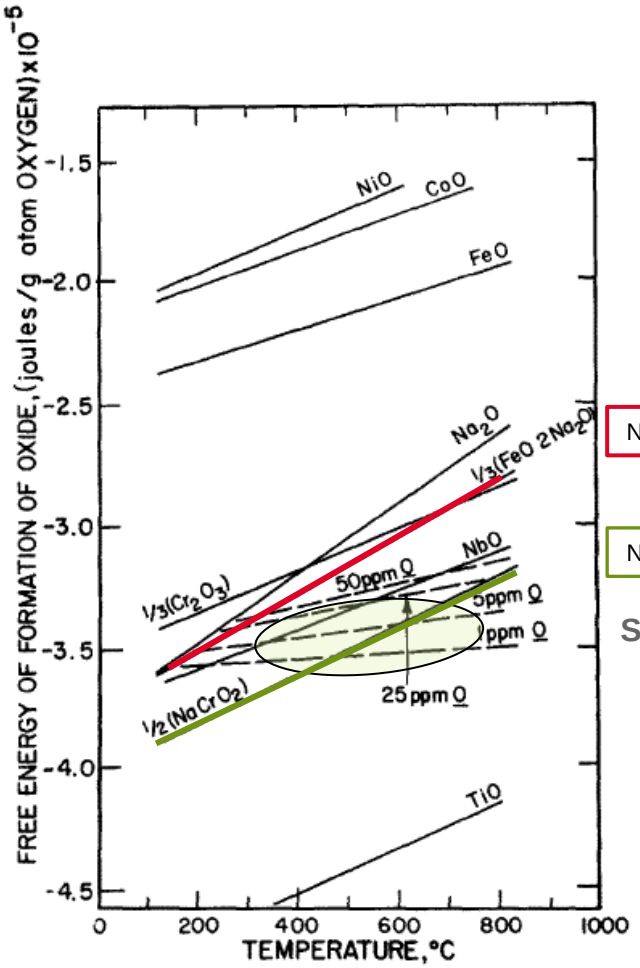


- **Plan :**
  the hypothesis will be supported by experimental results performed with laboratory scale setup to separate effects, and characterizations at the finest scale possible, and discussed as regards some literature results

  1. Alternate dissolution/oxidation thermodynamic zones
  2. Test at 550°C and low oxygen
  3. Discussions + some insights for corrosion modelling and reactor operation

2) ALTERNATE DISSOLUTION/OXIDATION THERMODYNAMIC ZONES 1/4

- Ellingham diagram for various oxide in liquid sodium at different oxygen content



Na_4FeO_3

$NaCrO_2$

SFR operating window

$4Na+O_2 \leftrightarrow 2Na_2O$

$$-RT.\ln\frac{{a_o}^2}{P_{O2}} = 2\Delta G^0_{f,Na_2O}$$

$$a_o = a_{Na2O} = \frac{\mathrm{Co}}{S_O}$$

$$\log S_o = \mathrm{a} - \frac{\mathrm{b}}{T}$$

$2Na_2O + Cr = NaCrO_2 + 3Na$

$${a_o}^2 \cdot a_{Cr} = \exp\frac{\Delta G^0_{f,NaCrO_2} - 2\cdot\Delta G^0_{f,Na_2O}}{RT}$$

➡ **The only potential oxide is $NaCrO_2$**

K. Natesan, 1975, MET. TRANS. Vol 6A pp1143-1153

Oxygen threshold for the $NaCrO_2$ formation vs. T and Cr activity of surface layer :

$2Na_2O + Cr = NaCrO_2 + 3Na$

$\Delta G^0_{f,NaCrO_2}$=-842258+189,06T

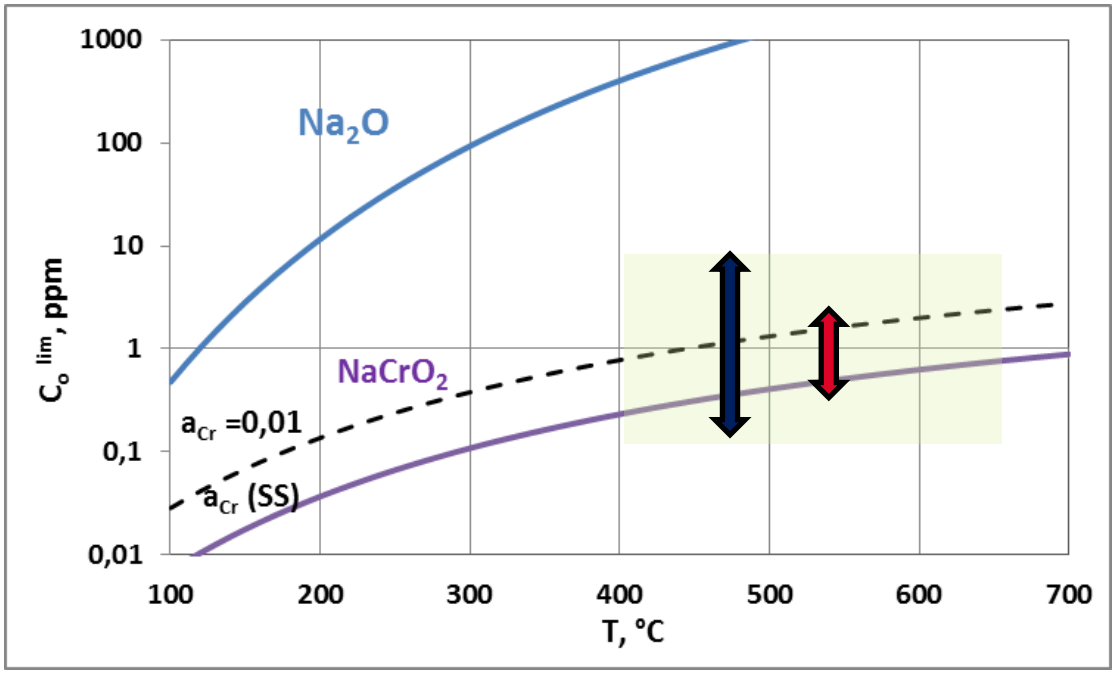
Bhat, Borgstetd, Werkstoffe und Korrosion 39,115-123(1988)

$$a_o{}^2 \cdot a_{Cr} = \exp \frac{\Delta G^0_{f,NaCrO_2} - 2 \cdot \Delta G^0_{f,Na_2O}}{RT}$$

$\Delta G^0_{f,Na2O}$=-421530+141,41T

$$log a_{Cr} = -0{,}577 + \frac{69{,}1}{T}$$

a_o =C_o^{lim} / Csat (Noden)



a_{Cr} ↘ C_o^{lim} ↗

Oxidation zone ↘

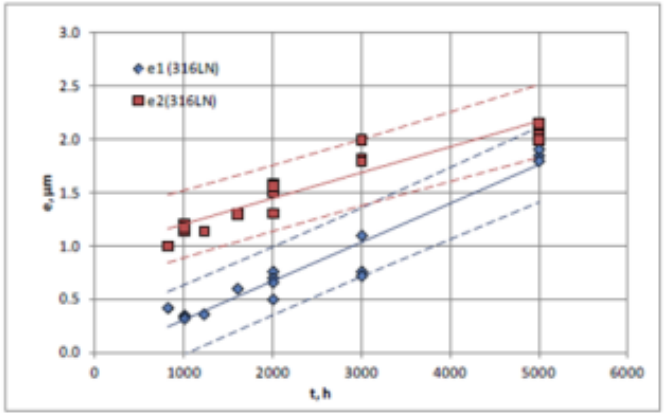
Dissolution zone ↗

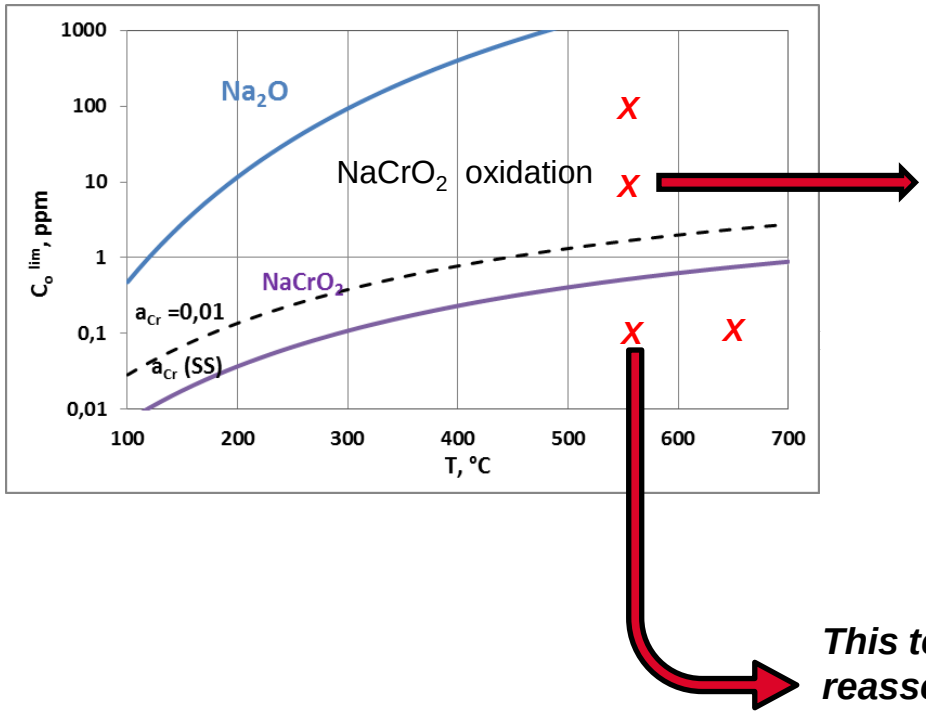
Alternate conditions possible by surface modification or coolant chemistry change

- Test achieved up to now at 550°C and 650°C - <1ppm, 40 ppm and 200 ppm in both oxidation and dissolution zones according to sodium chromite
- Weight gain for slight oxidation, kinetics assessment by GD-OES for 316L(N) and T91:

Oxide : $e_1(t) \pm 0{,}14 = -5{,}55.10^{-2} + 3{,}63.10^{-4} \cdot t$

Cr depleted zone : $e_2(t) \pm 0{,}14 = 0{,}966 + 2{,}41.10^{-4} \cdot t$

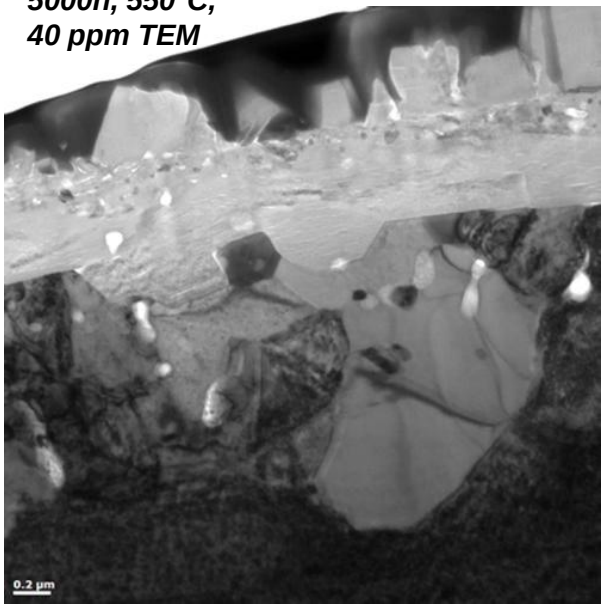




This test to reassess the dissolution

316L(N)
5000h, 550°C,
40 ppm TEM

Fast Reactors, 2013

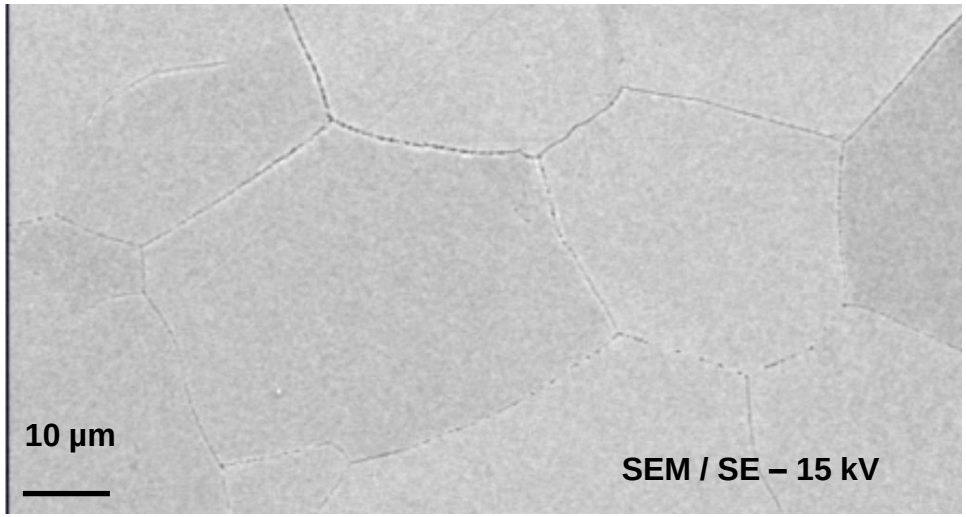


316L(N) : grade X2CrNiMo17-12-2

- Nitrogen controlled, elaborated in accordance with the RCC-MR codification (RM 3331 level 2). After rolling, the steel was annealed at 1120°C and quenched in water.
- Mean grain size is between 30 to 40 µm
- Electrical discharge machine (EDM)

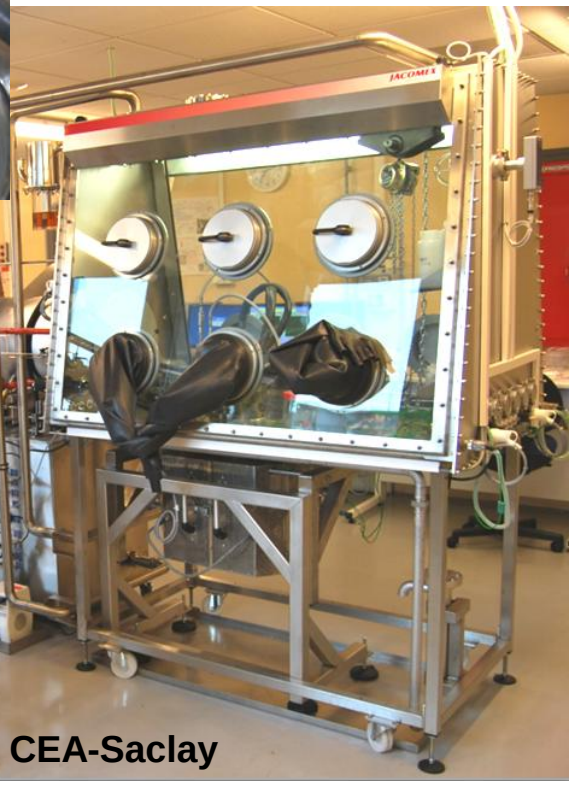
TABLE I
Composition of the 316LN stainless steel tested.

Element	Concentration (wt. %)
Fe	Balanced
Cr	17.27
Ni	12.13
Mo	2.54
Mn	1.74
C	0.026
Si	0.31
P	0.025
S	0.001
N	0.069
B	0.0004
Cu	0.0029
Co	0.09

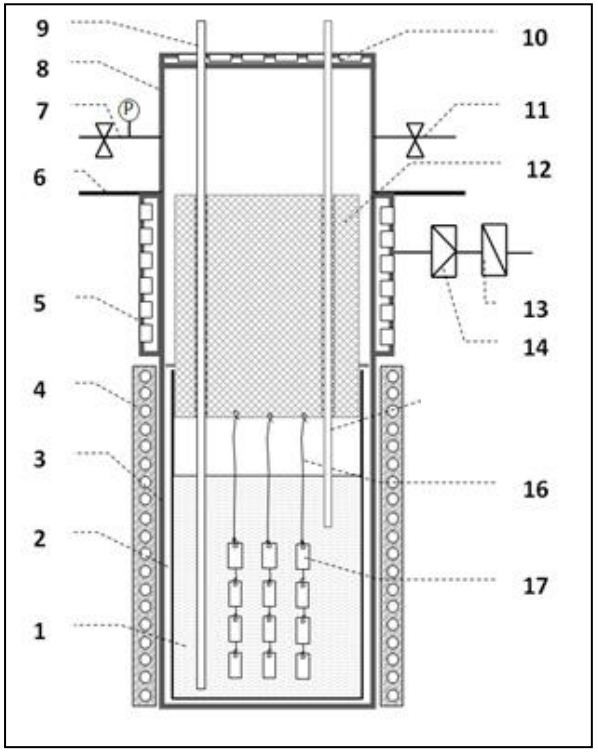


▪ Liquid metal setups : CORRONa (as Corrosion sodium) α + β

- Closed and tight system
- Ar purified glove-box
- Mo-crucible
- 2.3 kg Na
- Safety (double barriers)



CEA-Saclay

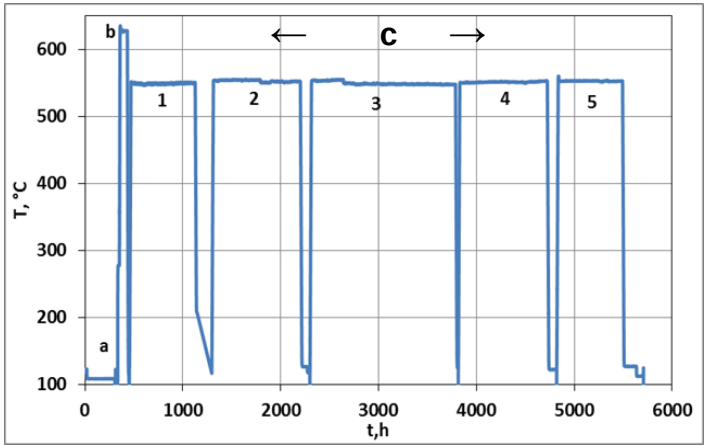


1- Liquid sodium, 2- Molybdenum crucible, 3- Thermal well, 4- Oven, 5- Cooling channels, 6- Gloves box floor, 7- Gas inlet and pressure monitoring, 8- Well cover, 9- Temperature well, 10- Upper cover cooling section, 11- Gas outlet, 12- Sodium vapor reflux condenser, 13- Aerosols filter, 14- Bursting disks, 16-Molybdenum wires, 17- Corrosion specimen

Icapp-2011

- **Corrosion Tests : 550°C in static sodium for 4577 h for low oxygen condition (<~1 wppm)**

a) Preconditioning (melting, settling for 300h at 108°C, skimming out residual oxide at free level)
b) Zirconium foil purification (75 h at 628°C, 9 dm²)
c) Exposition in Na for step 1 to 5
   one sample in and one out
d) Ethyl alcohol , then pure water quick cleaning + desiccator storage
e) Weight variation - SEM /EDS – GD/OES – FIB/TEM (HRTEM, EDX, EELS)



316LN steps	Exposure duration, h				
	1	2	3	4	5
8P	657				
8Q	→	1549			
8R	→	→	3023		
8S	→	→	→	3918	
8T	→	→	→	→	4577
8U	→	→	→	→	4577
8V		→	→	→	3920
8W			→	→	3028
8X				→	1555
8Y					659

- Others samples tested at the same time : Fe-9Cr-1Mo, A800, Fe, Ni, Hf, Al_2O_3, HfO_2

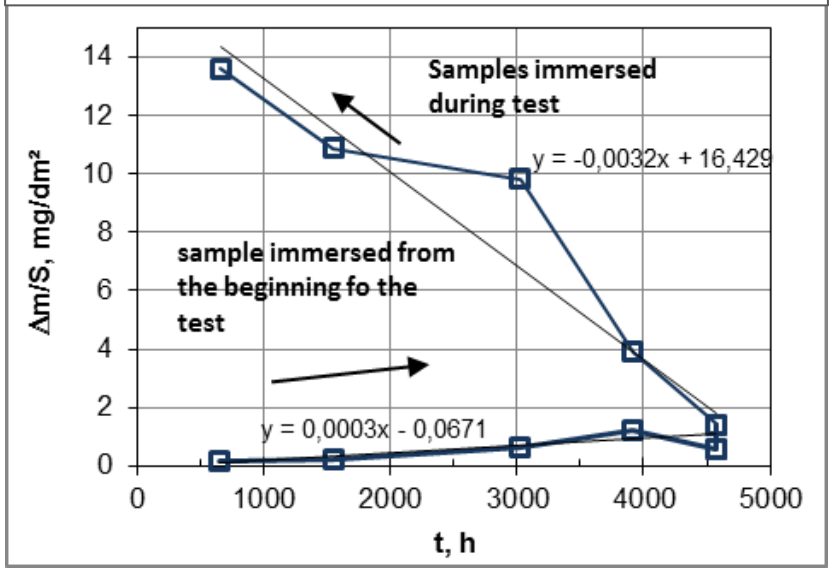
4) RESULTS - WEIGHT VARIATION

Weight variation + Macroscopic examination

- Cleaning : weight gain after ethanol cleaning higher than after water cleaning, meaning sodium remains in the porosities present in the corrosion surface layer
- Sample immersed from the beginning, weight gain small but not null: + 0,006 mg/dm²/d (if supposed linear)
- Up to 100 times larger weight gain for 650h for the same duration

8P - 657 h	8Q - 1549 h	8R - 3023h	8S - 3918 h	8T+8U - 4577 h
				
				
8Y - 659 h	8X - 1555 h	8W - 3028 h	8V - 3920 h	

Weight variation after water cleaning

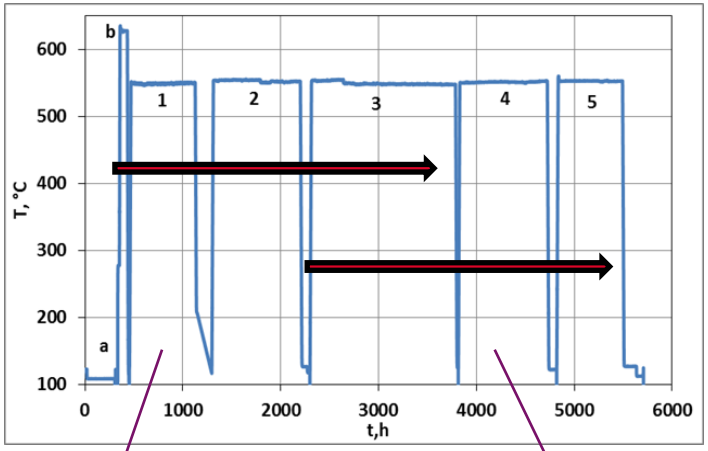


- Conclusion : from 2 to 28 mg/dm²/y on the corrosion kinetics based on weight variation

4) RESULTS - 2 DISTINCT BEHAVIORS

3025 h (1500h in Common) :

Δm/S : +0,67 // + 9,63 mg/dm² **ratio 14**



8R- 3023 h

8W – 3028h

- **Conclusion :** 2 totally distinct behaviors observed even though sample were exposed for common periods, then to the same liquid metal chemistry,

But

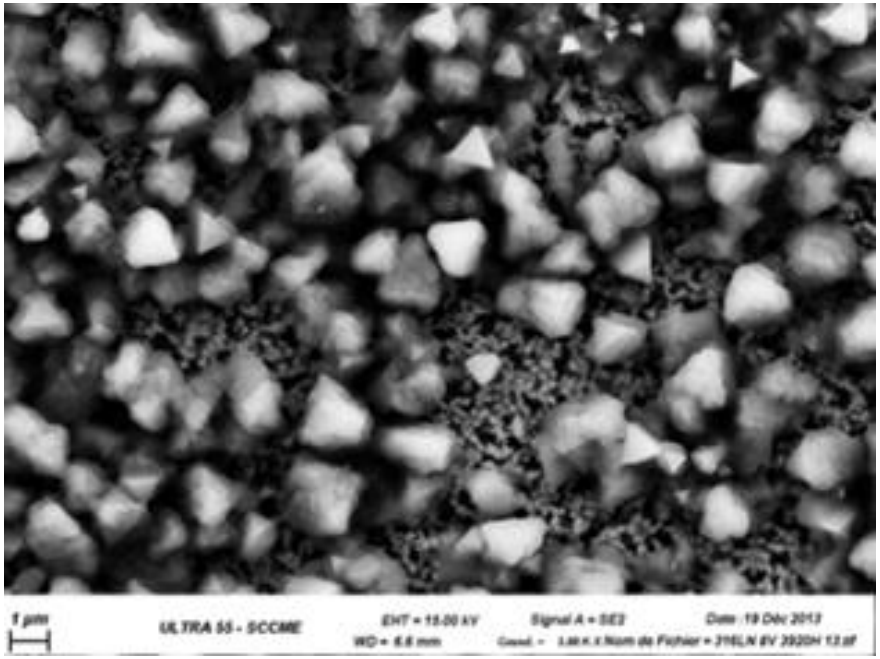
some were exposed from the beginning
others immersed during the test

→ **Oxidation + 'Dissolution' (carburization) can happen at the time?**

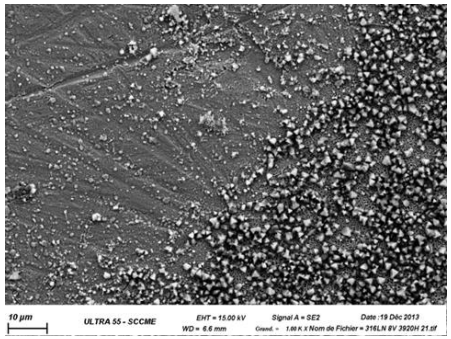
Oxidation characterization : SEM

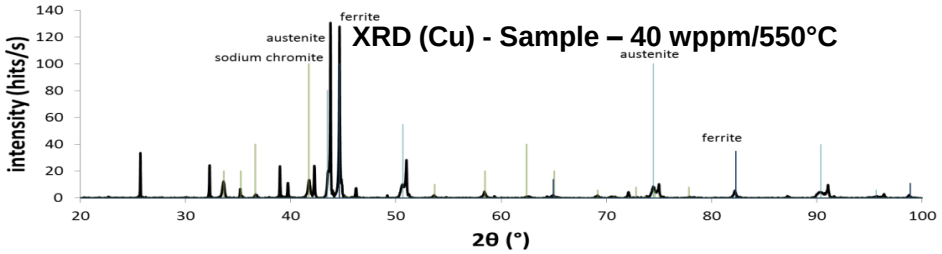
- Zone 2 : black patches that expand for the last period
- Crystallites enriched in Na, Cr and O (1µm – triangular shape)

SEM surface observation (SE) of zone 2 last 3900 h (periods 2+3+4+5) of the test



Transition 1-2

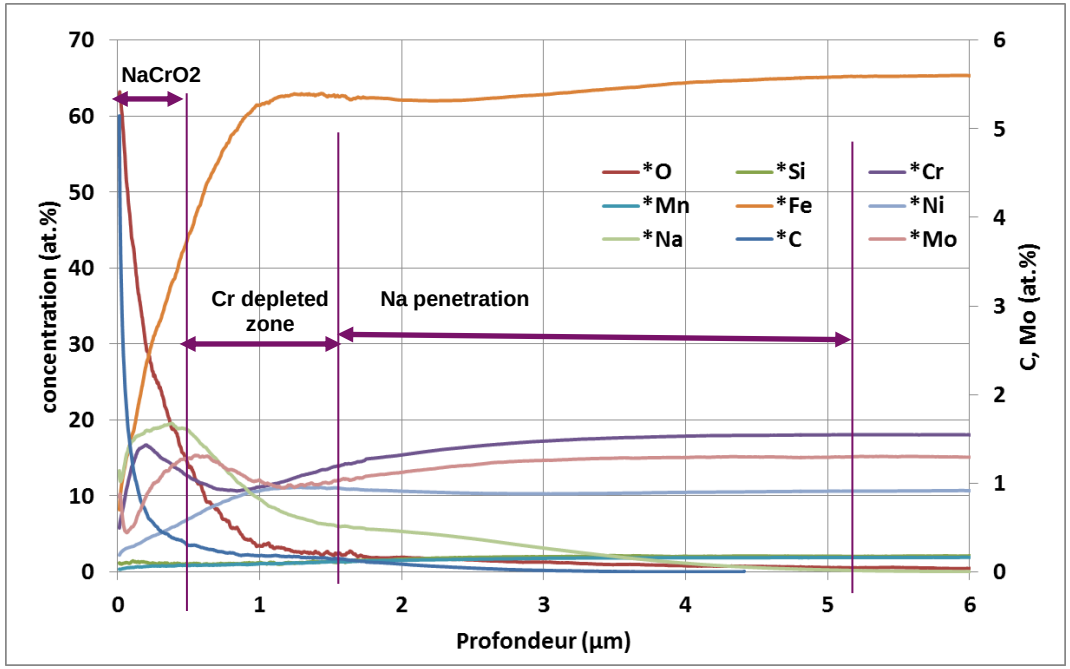




Conclusion : zone 1 = sodium chromite oxide scale ($NaCrO_2$)

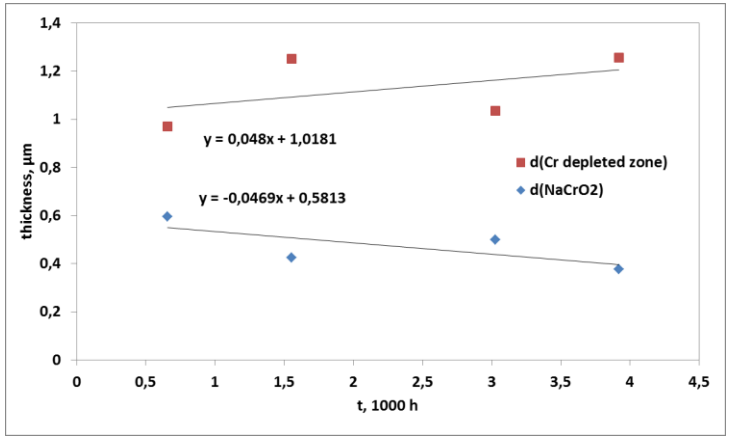
Oxidation characterization : GD-OES

- Oxide scale (Na-Cr-O) : 500 nm, not function of exposure duration
- Cr depleted zone : 1 µm thickness steady with time (no Ni leaching<-> Fe), porosities, carburization zone which is more intense and larger than the one caused by EDM machining, some indications of internal oxidation (SiO_2)
- In between : a Mo enriched zone, 0.1 to 0.2 µm
- Sodium profile extends to 4 to 6 µm in depth : sodium penetration zone ?



GD-OES zone 2 - last 3900 h (periods 2+3+4+5) of the test

Thickness's evolution



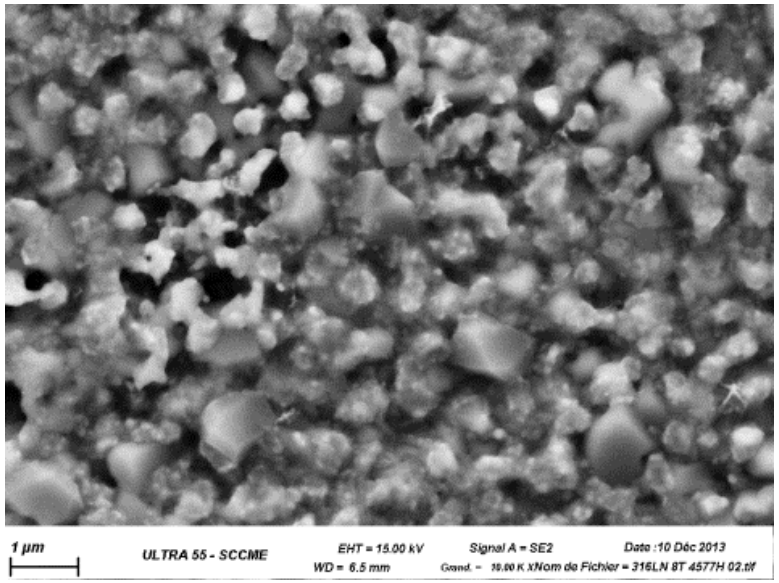
- Conclusion : steady thickness but surface extends for the last exposure period even though durations are shorter

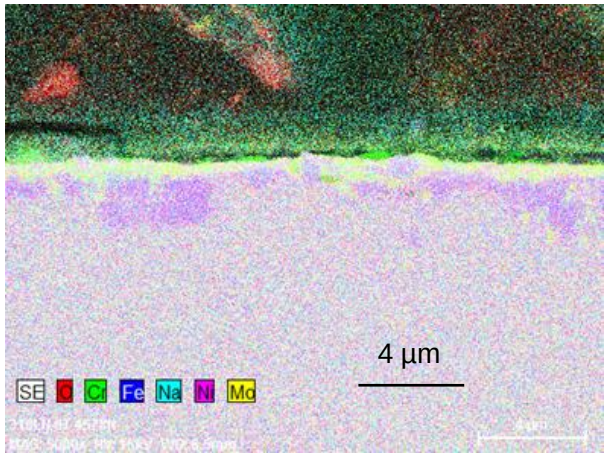
Oxide scale formation lead to a Cr chemical activity at the surface layer lower than the bulk

‘Dissolution’ characterization: SEM

- No apparent evolution with exposure duration, with quasi-null weight gain
- Porosities ~500nm (Mo enriched) -> coral like structure
- Crystallites (250 nm to 1 µm, Fe, Cr or Cu rich)
- Na penetration

SEM surface observation (SE) 4577 h (periods 1+2+3+4+5)



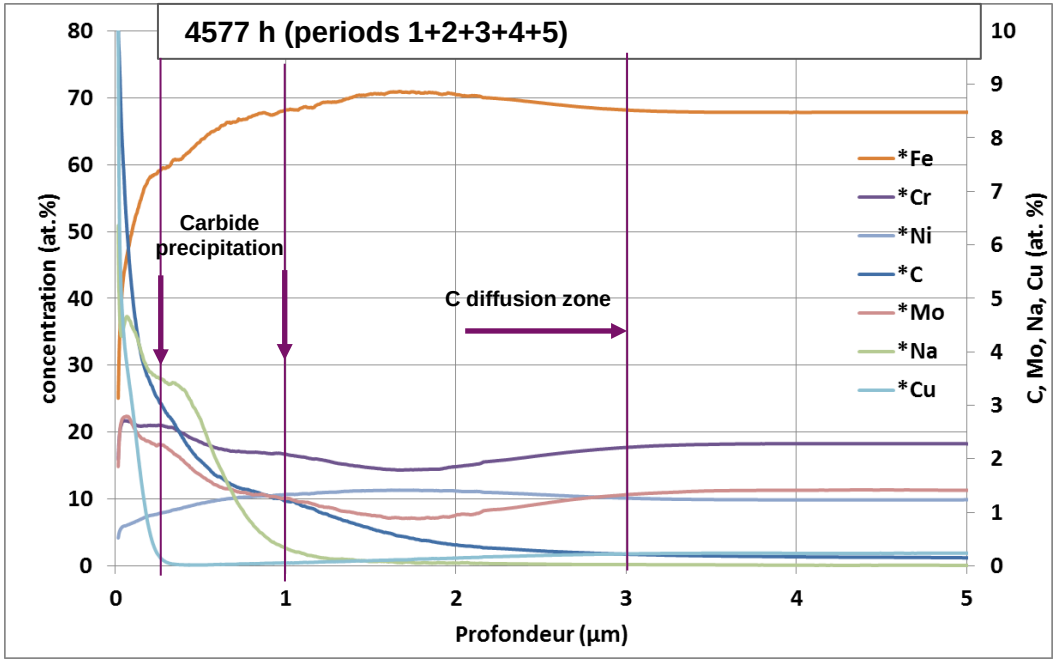


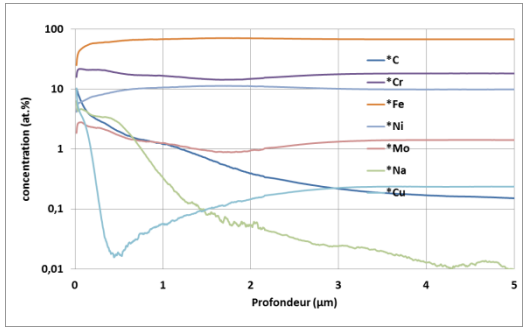
Cross-section: Cr depleted zone, Mo enriched at the interface, Cr rich particle's at the surface

Conclusion : - No oxide present
- little and homogenous corrosion (porous zone + crystallites formation)

Dissolution' characterization: GD-OES

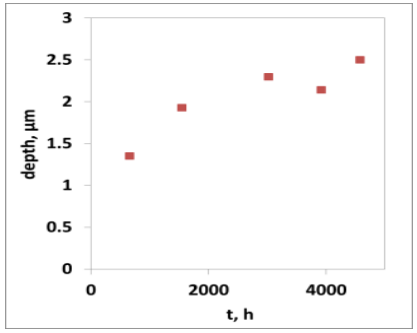
- No oxygen except surface contamination
- Carburization: precipitation of carbides $(Fe, Cr, Mo)_xC$ and diffusion profile up to 3 µm for 4577h
- Mo and Cr depletion zone, roughly steady after 3000h to 2-2,5 µm
- Na penetration but limited to porosities present in the surface layer (size seems to increase with exposure duration)
- Cu : dissolution (up to 2,5-3µm at 4577h) and surface precipitation ($s_{(Cu)}$=55 wppm –precipitation)





Log. Scale

Extent of Cr depleted zone (thickness for 90% of %Cr bulk)

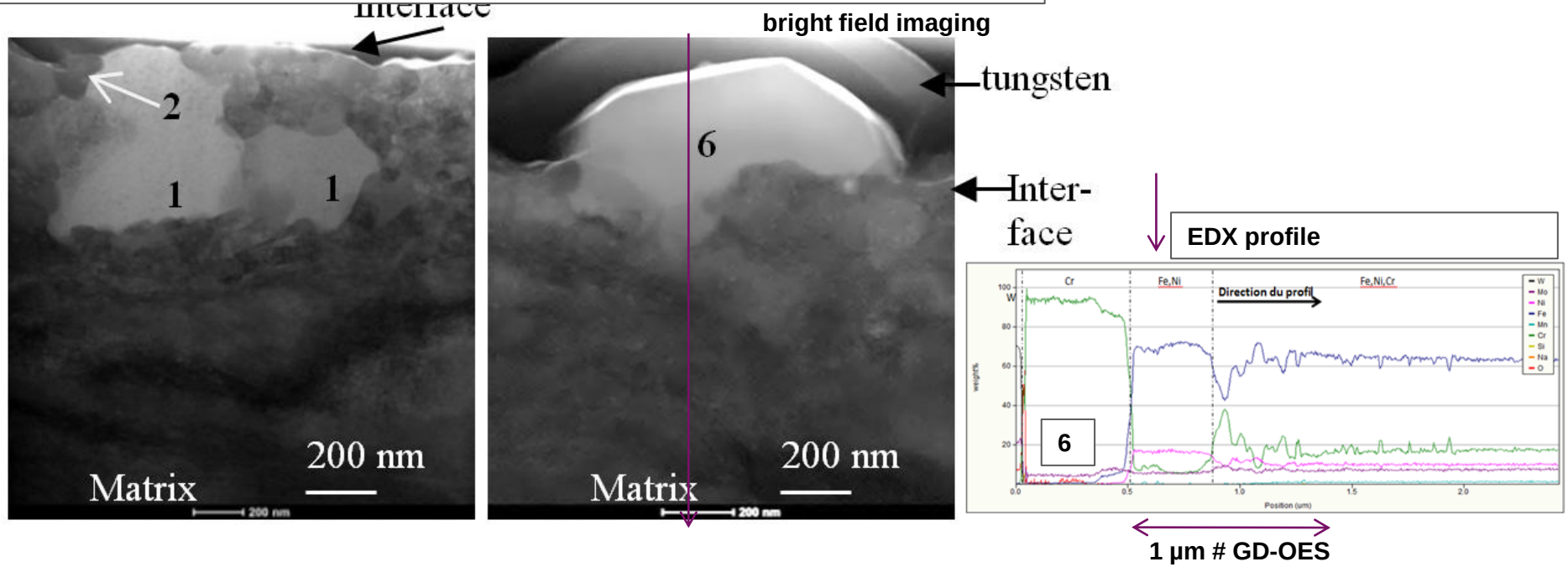


Conclusion: Carburization + dissolution evidenced but superposition of the phenomena, Dissolution of Fe and Ni leading to cavities and to Mo rich nodules formation (Cu = marker)

TEM characterization:

1. 90% Fe-rich grains of 400-800 nm in size in the surface layer, most probably ferrite
2. Mo-rich grains of 200 nm in size at the interface, which may be carbide or Chi intermetallic phase
6. Chromium carbide (EELS)

4577 h (periods 1+2+3+4+5) – Focused ion beam thin slice extraction



Conclusion: carbide precipitation at surface and in the Cr depleted zone, leading to a Cr chemical activity at the surface layer lower than alloy bulk activity

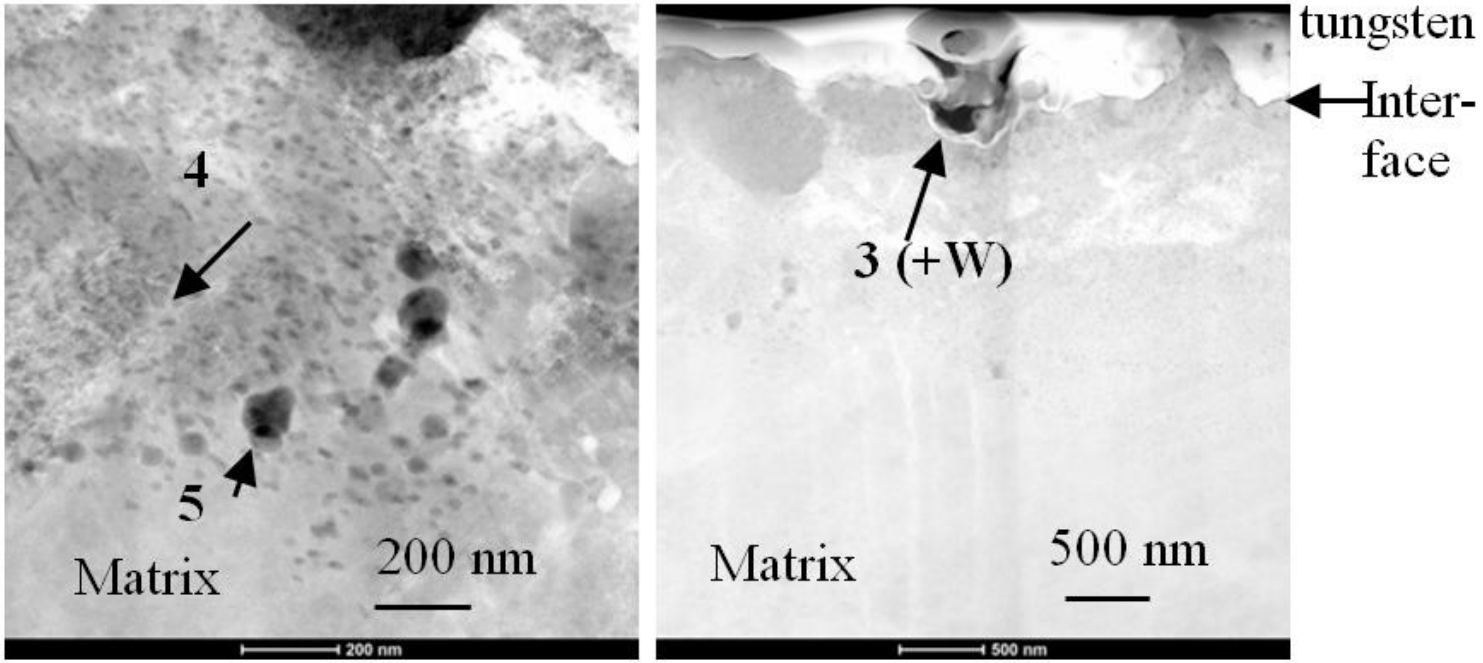
- 1st stage of ferrite scale formation as indication of Ni preferential dissolution of Cr depleted zone to be further studied

TEM characterization:

3. Porosities of 500 nm in size, which may be grains ripped off during sodium test or sample preparation
4. 10-50 nm inclusions in the Cr depleted zone, rich in Si and O (ratio ½) = internal oxidation with SiO_2 formation
5. Cr-rich spherical inclusions of 100 nm in size, which are intra-granular Chromium rich carbide and are noticeably absent from ferrite grains

4577 h (periods 1+2+3+4+5)

High angle annular dark field imaging



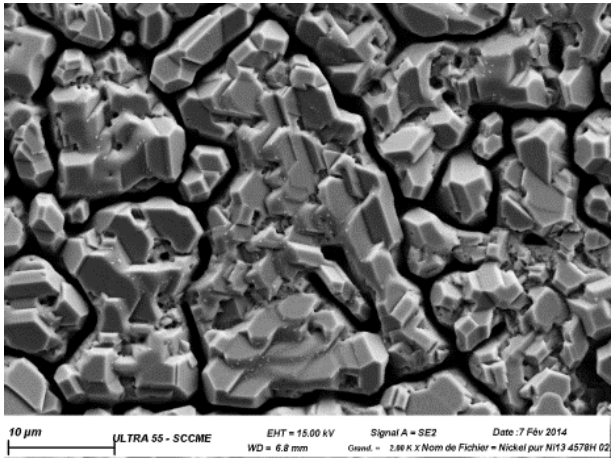
- **Conclusion : internal oxidation as marker of oxidation transient = open issue**

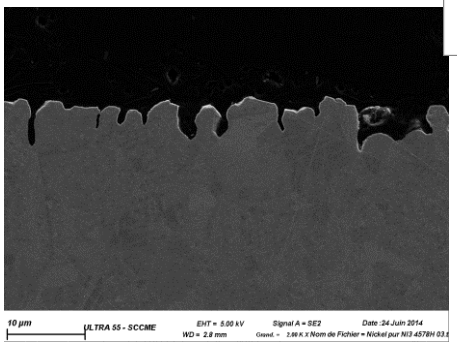
4) RESULTS - FE AND NI PURE METALS

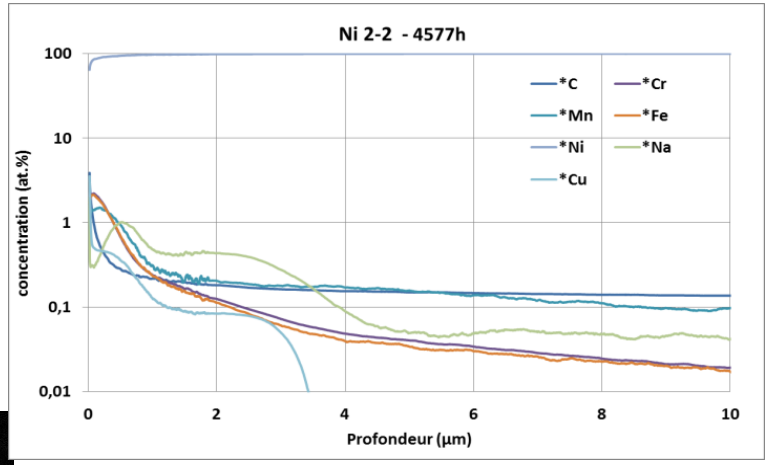
Dissolution : negligible at 550°C, as observed with pure metals of the same test

Ni : +0,1 mg/dm²/d - weight gain – Fe mass transfer - Na porosities - deposition

Ni – 4577h







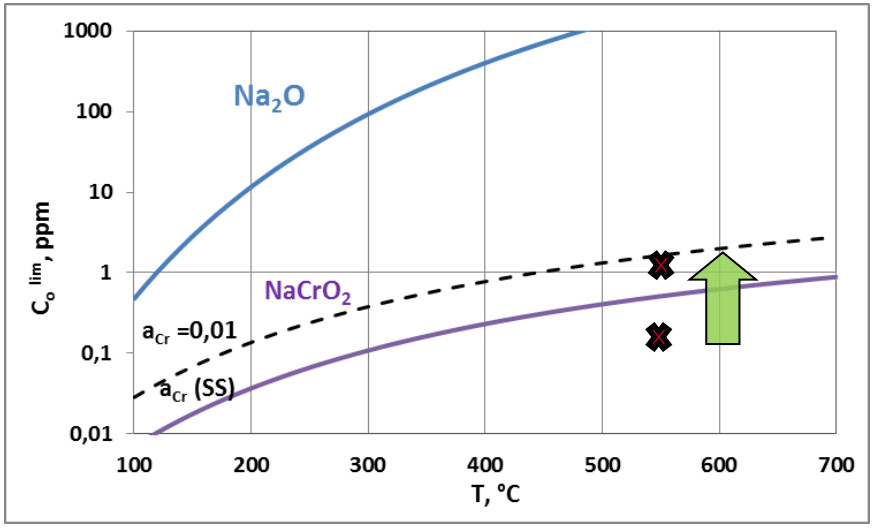
- **Mass transfer did occur in between sample function of surface layer activities**
- **Cu : dissolution + precipitation**

5) DISCUSSION - LIQUID METAL CHEMISTRY 1/4

1- Liquid metal chemistry evolved during test :
- Carbon: initially high in new Na, decreased by reaction with materials
- Oxygen: initially low, gradual increase at each opening for sample extraction and immersion at 110-120°C (no continuous Zr getter) (1-5 ppm max,)

2- Oxidation and carburization : lower surface layer a_{Cr} that increases a_o^{min} for oxidation

3- Dissolution happened but negligible



a_{Cr} ↘ C_o^{lim} ↗

Oxidation zone ↘

Dissolution zone ↗

Sample immersed from the beginning

1- [O] initially low, high [C], carburization occured

2- a_{Cr} decreased due to carburization that increased a_o^{min} for oxidation

3- [O] increased with testing time but not enough to exceed a_o^{min}

4- Dissolution happened as well

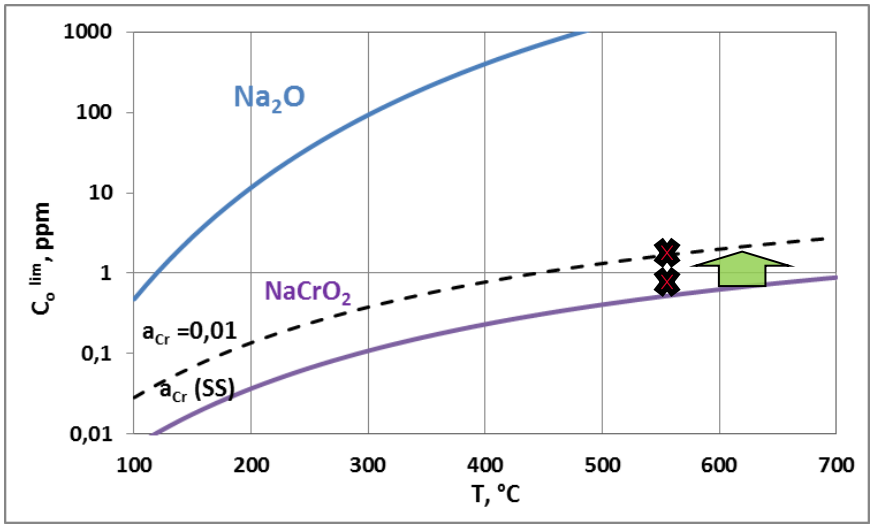
Sample immersed during the test

1- [O] slightly higher to exceed a_o^{min} , low because of new unaffected sample, [C] lower

2- a_{Cr} decreased due to oxidation that increased a_o^{min}

3- The oxidation driving force is larger for the late specimen, where [O] and a_{Cr} presented probably their highest values

4- Sodium chromite might have been slightly dissolved or reduced for prior oxidized specimen when compared to late specimen



a_{Cr} ↘ C_o^{lim} ↗

Oxidation zone ↘

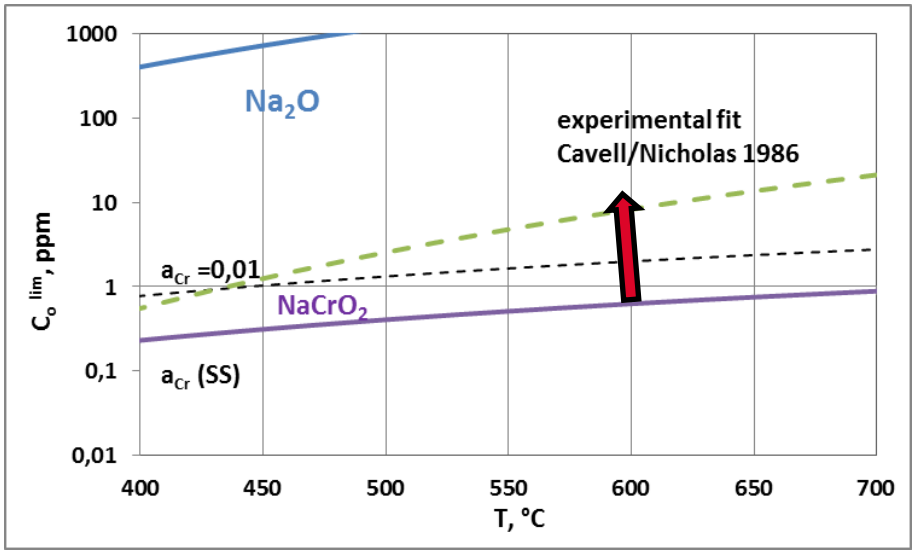
Dissolution zone ↗

Conclusion :

This test demonstrates that liquid metal chemistry combined to surface layer evolution changed thermodynamic threshold for oxidation that explain alternate oxidation/dissolution behavior observed in this test

This interpretation agrees with experimental results obtained in sodium loops

- Cavell & Nicholas 1980 – experimental fit for higher than expected C_o^{lim}
- Unexplained initial weight gain followed by weight loss in specimen exposed to HT section of a loop (oxidation – reduction)
- Sodium aged specimen less prone to oxidation as dissolution zone is enlarged (Crouch-1978)



5) DISCUSSION - SYSTEM OPERATION 4/4

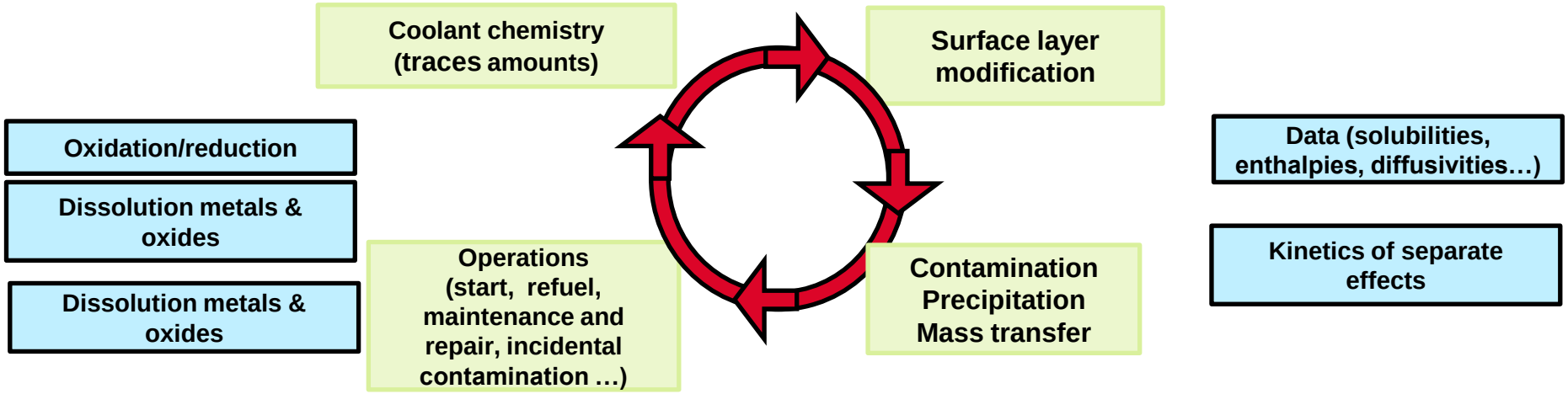
- New surface more prone to oxidation for little contamination (5 ppm) when compared to aged surfaces
  - ⇒ all of available oxygen concentrate on smaller surface giving larger than expected oxide scale
    - Refuel – component handling – maintenance and repair
- For a closed anisothermal system, oxygen will be buffered with time at a very low concentration by the low T equilibrium with $NaCrO_2$, causing oxide reduction in the medium and high T section of the loop
- Long term corrosion prediction could be improved by taking into account alternate phases of oxidation/reduction over service life time

5) CONCLUSIONS – CORROSION MODELLING

- Corrosion is the results of a number of competing mechanisms that affect the surface layer of the material as well as the coolant chemistry

  Oxidation+ carburization mass transfer dissolution

- Thermodynamics defines the reaction paths vs. chemical potentials
- Models => multicomponent systems with retrofit loops due to traces evolution of the liquid metal chemistry caused by the corrosion processes to take into account the complexity



Thank you for your attention

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