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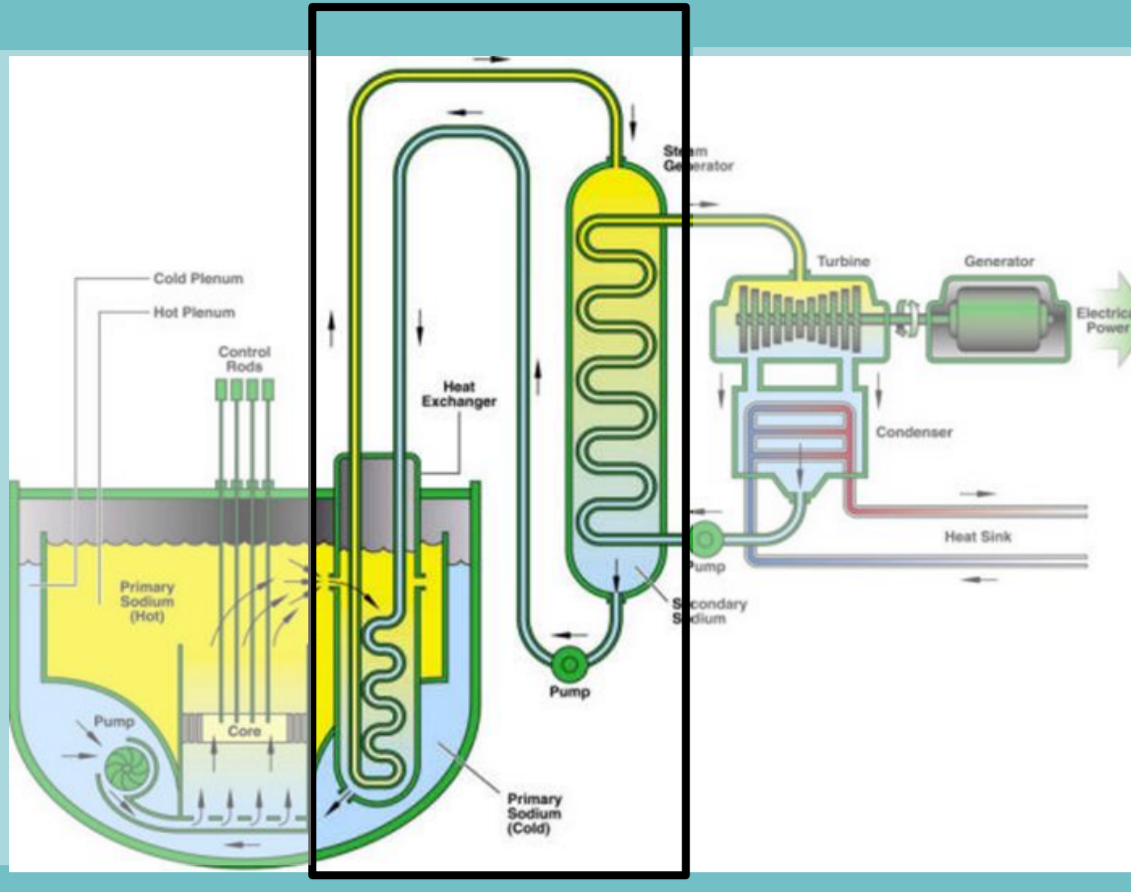
Corrosion Behavior of a AISI-316 Stainless Steel Grade Type in Nitrogen Environment for a Sodium Gas Heat Exchanger

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CONTEXT: Generation IV for nuclear power plants: Energy Conversion System for ASTRID project



Energy Conversion in nuclear plants uses to be operated by steam generators. To eliminate the Sodium-Water Reaction Risk, an alternative option of Energy Conversion System operating with gas is developed in the framework of ASTRID project. Heat of the nuclear reaction is recovered by a secondary sodium system and transferred to a 3rd circuit containing **Nitrogen** and maintained at 180 bar to make the turbine rotate.

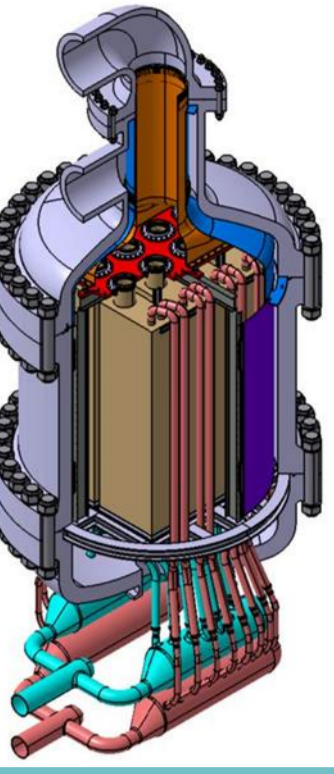
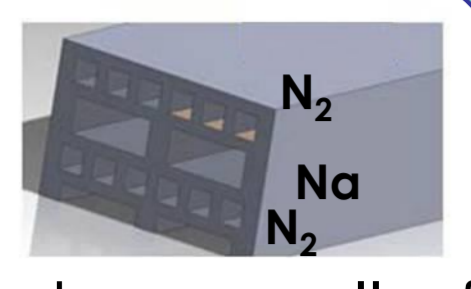
In **Sodium-Gas-Energy Conversion System**, heat transfer takes place inside modulus comprising 2 channels networks: one for nitrogen and the other one with larger section for sodium flowing. Each channels are separated by a wall of 2 mm thick for good thermal conductivity.

Selected material : AISI- 316 SS grade

Working conditions in the modulus:

Na: P ~1bar ; Inlet $\theta=530^{\circ}\text{C}$ and Outlet $\theta=330^{\circ}\text{C}$

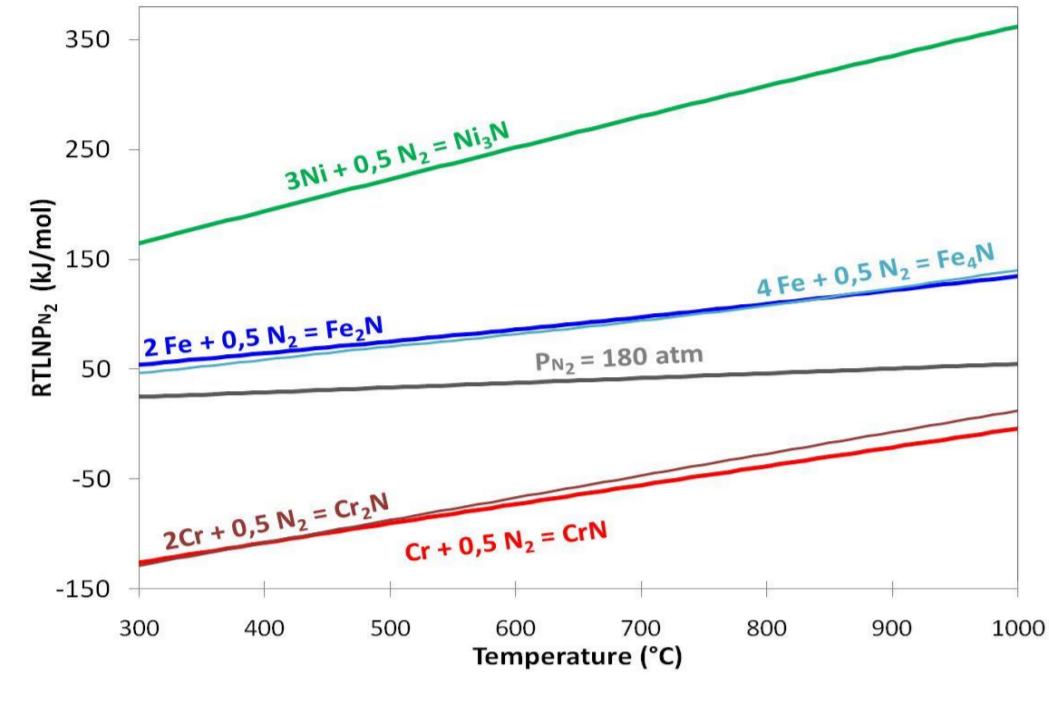
N₂: P=180 bar ; Inlet $\theta=315^{\circ}\text{C}$ and Outlet $\theta=515^{\circ}\text{C}$



OBJECTIVES

Good performance of the ECS has to be guaranteed for **30 years** → Compatibility of the 316L with N₂ environment at 515°C and 180 bar has to be checked.

Stability of main nitrides as a function of P_{N₂}. Activity values of Fe, Cr, and Ni are the molar fraction in 316L. At 515°C and 180 bar N₂, CrN and Cr₂N are potentially formed.



→ Expected phenomenon :

• Nitrogen diffusion onto the surface

→ **nitriding layers;**

• No continuous layer

→ **internal nitridation** (in the matrix).

Severity of damages depends on affected thickness.

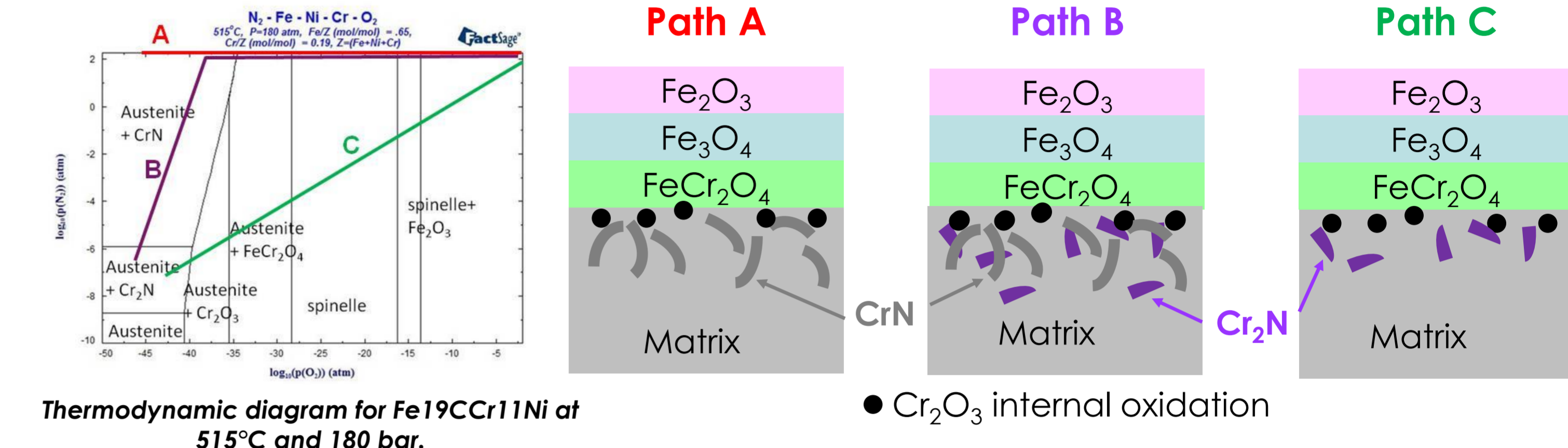
→ Few relevant data within the ECS conditions :

they concern other environment than pure N₂ (NH₃, N₂/air or complex atmospheres), other materials (Ni-based alloys) and higher temperature.

If oxygen is present, competition between nitridation and oxidation may occur.

Oxidation susceptibility to take into account.

Considering that both P_{N₂} and P_{O₂} decrease in serial corrosion layers from external to bulk material, thermodynamic diagram suggests 3 scenarios:



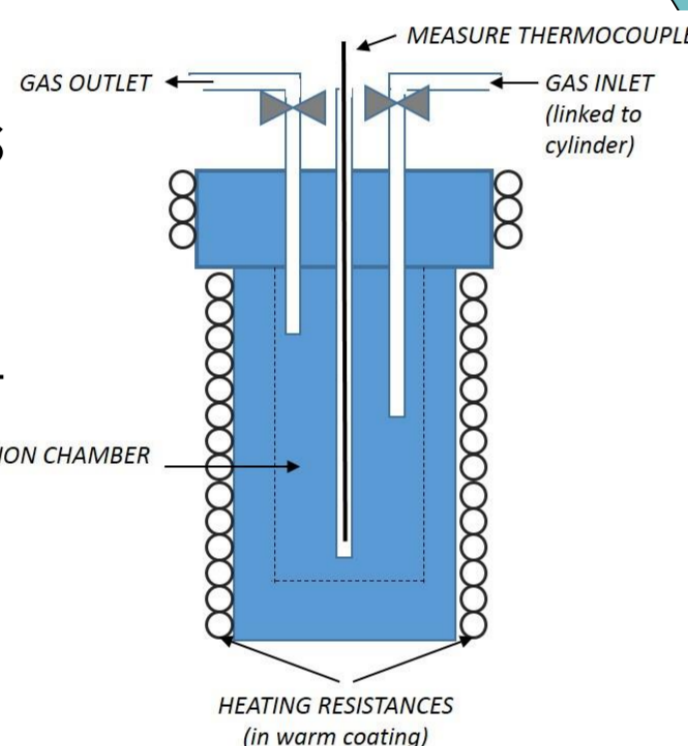
Thermodynamic diagram for Fe19Cr11Ni at 515°C and 180 bar. Obtained with FaciSage.

Literature do not rule on the absence of damaging on 316L in ECS conditions. Experimental program set up to acquire long term corrosion kinetics (up to 5000 hours)

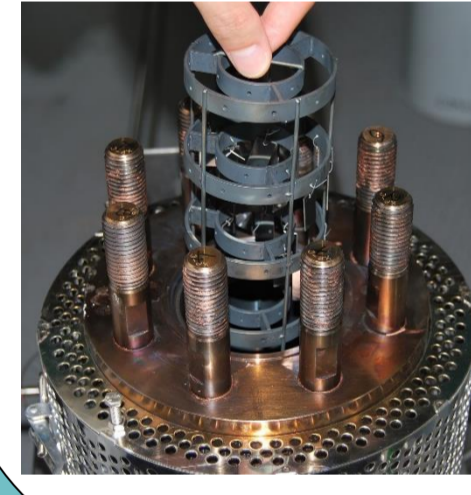
EXPERIMENTAL

STATIC UNDER PRESSURE TEST (P = 180 bar)

- Cylindrical pressure sealed vessel with up to 40 samples hung up to holder;
- Filled with 67 bar industrial N₂ (4.5) at RT and heated at 515°C for variable cumulative durations : 100, 300, 500, 1000, 200,2500, 3500, 5000 and 5500 hours after initial starting;



- Samples withdrawing after heating stop and gas purge;
- New samples introduced in-between;
- Corrosion kinetics evaluated by weighting before and after test.



MATERIAL

The design of this ECS module is innovative with a specific fabrication route. A module consists of a stacking of 4 mm thick sheets welded together by diffusion activated by Hot Isostatic Pressure. Test coupons are sampled in a module mock-up so as to have welding junctions within the samples. Material tested is **1.4404**.

C	Si	Mn	P	S	Cr	Mo	Ni	N	Co	Fe
0,022	0,335	1,286	0,034	0,002	16,543	2,044	10,093	0,048	0,132	bal

Composition (weight %) of studied material

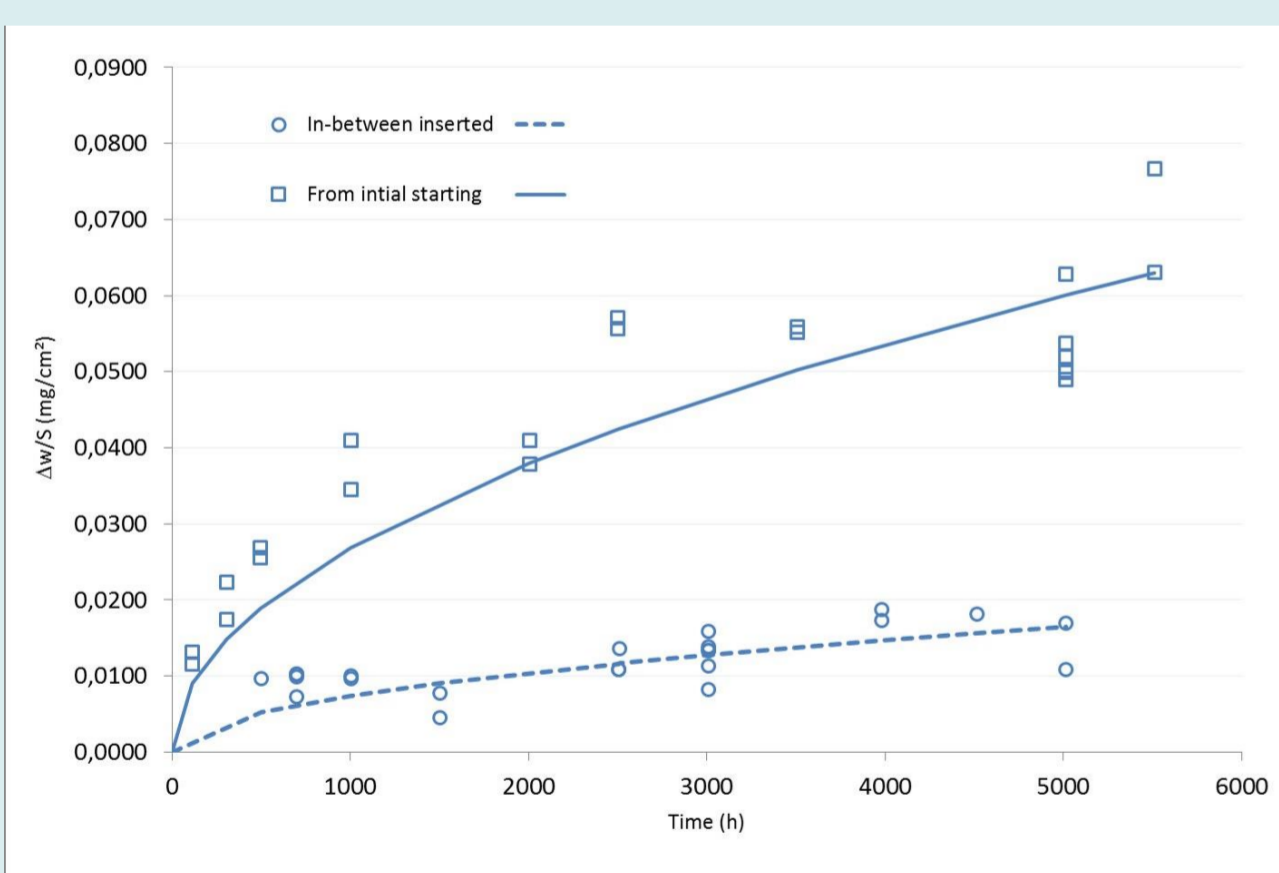
RESULTS

KINETICS

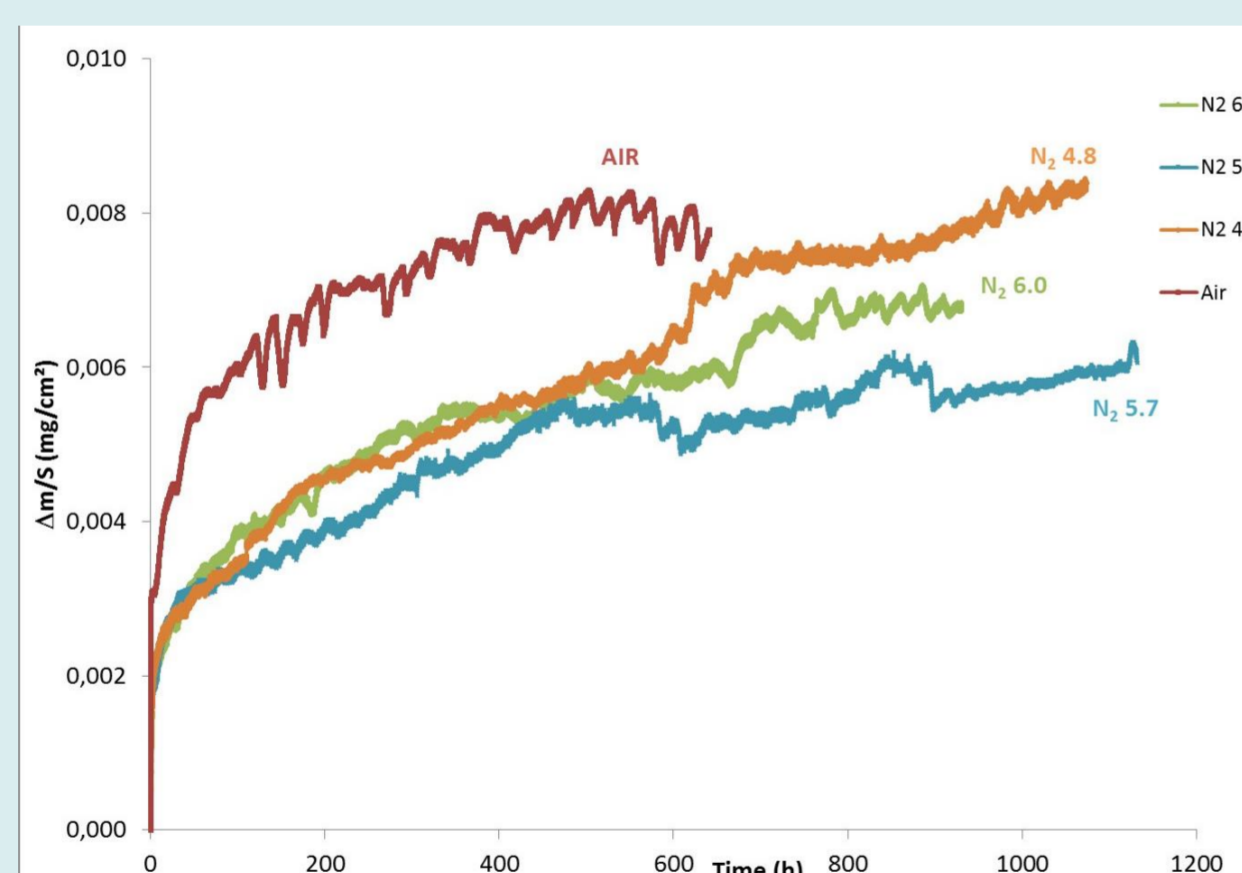
- Parabolic kinetics in both environment : $\frac{\Delta m}{S} = \sqrt{k_p t}$.
- Static test : 2 well-marked kinetics which depend on introducing time;
- Dynamic tests : no influence of N₂ purity in range tested;
- Lowest kinetic obtained in static test = kinetics obtained in dynamic tests.

DYNAMIC TEST (P=1 bar)

- In a symmetrical thermogravimetric system (Setaram® TAG24);
- Gas linear flow rate = 2,2 cm/s at 515°C;
- 3 qualities of N₂ : with 20 ppm, 3 ppm and 1 ppm of impurities;
- Continuous mass gain acquisition;
- PO₂ measured by a zirconia probe mounted at the nearest of the sample;
- One single sample by experiment;
- Air environment is also tested.



Surfacic weight gain vs exposure time in static 180 bar N₂ 4.5 at 515°C

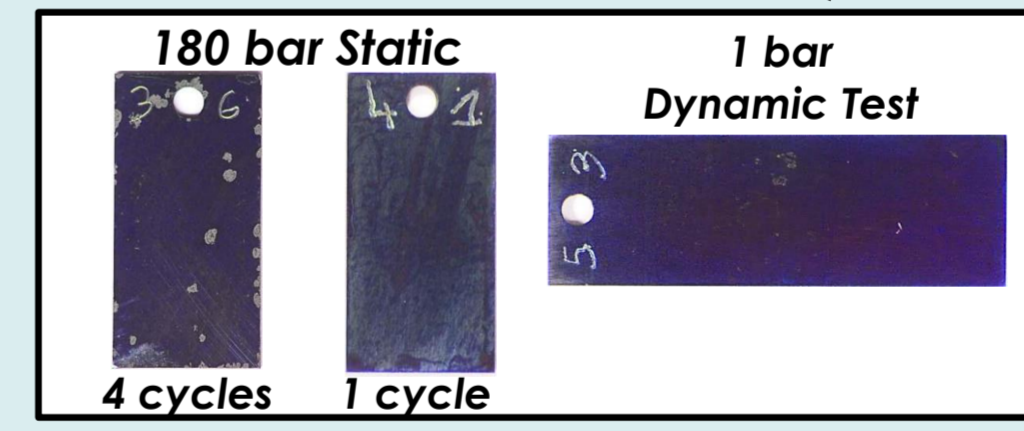


TGA curves at 515°C for different purities of N₂

Gas purity	PO ₂ (atm)	k _p (mg ² .cm ⁻⁴ .h ⁻¹)
Dynamic data		
N ₂ 4.8	9.10 ⁻⁵	6.1.10 ⁻⁸
N ₂ 5.7	2.10 ⁻⁶	2.9.10 ⁻⁸
N ₂ 6.0	1.5.10 ⁻⁶	4.7.10 ⁻⁸
Air	0,20	9,2. 10 ⁻⁸
Static data		
N ₂ 4.8	3.10 ^{-4*}	5,4.10 ⁻⁸
		7,2.10 ⁻⁷

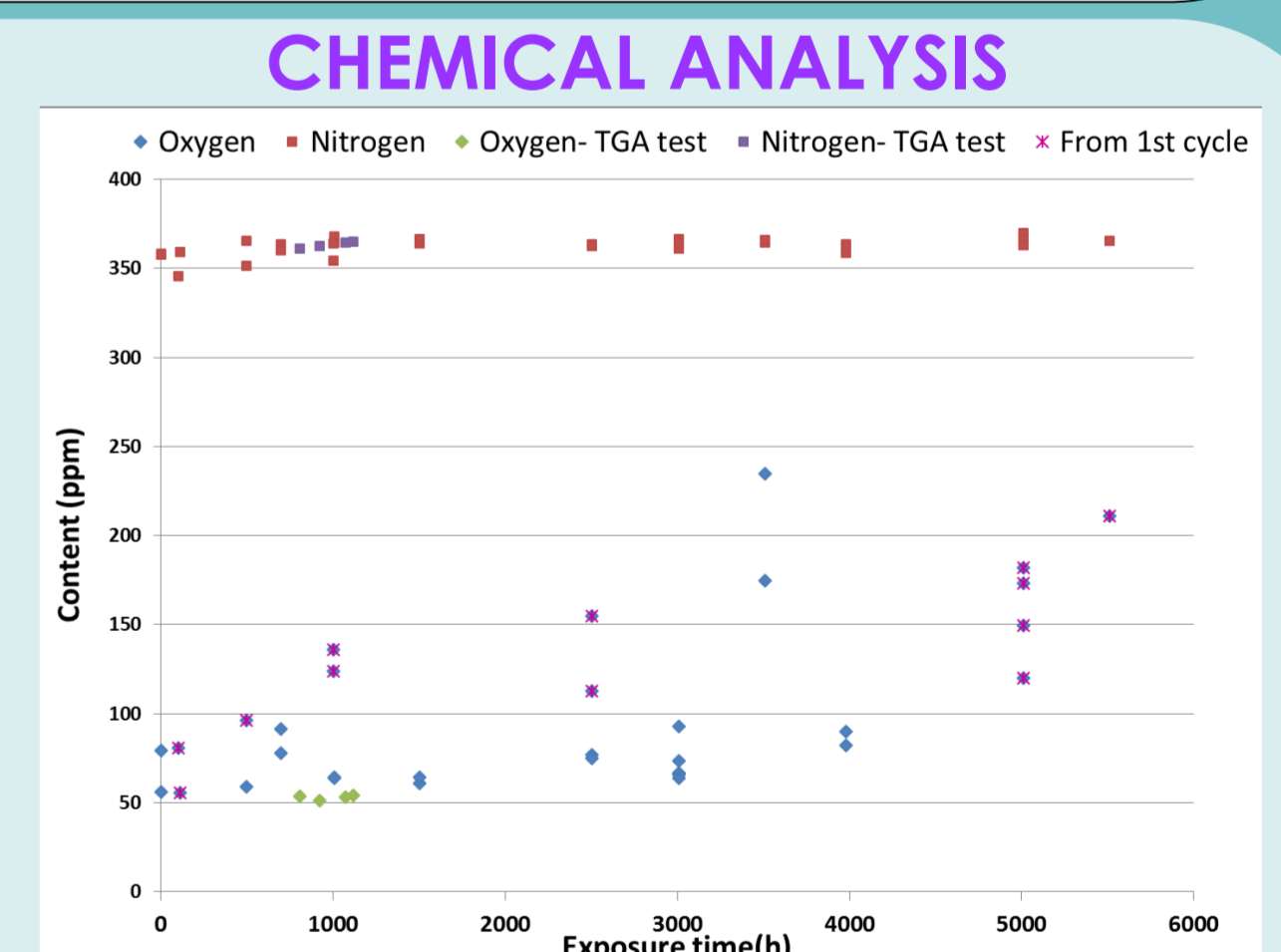
* onset value

- Differences of visual appearances according to different kinetics ;



Appearance of samples after 1000 h testing

- No growth of N global content with time;
- Well-marked increase of O global content.



Evolution of O and N content for all exposure conditions. Analysis by inert gas fusion technique

SURFACE MICROSTRUCTURES

- Comparison of surfaces after 1000 h (cumulated or continuous) exposure

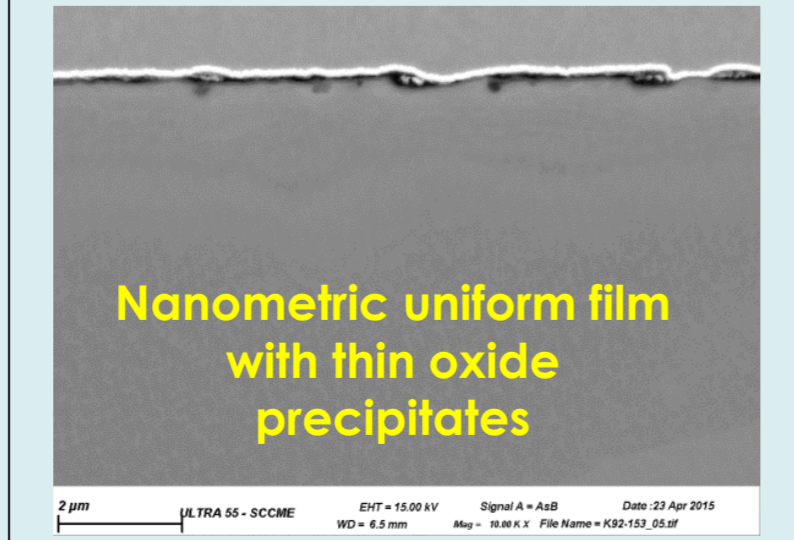
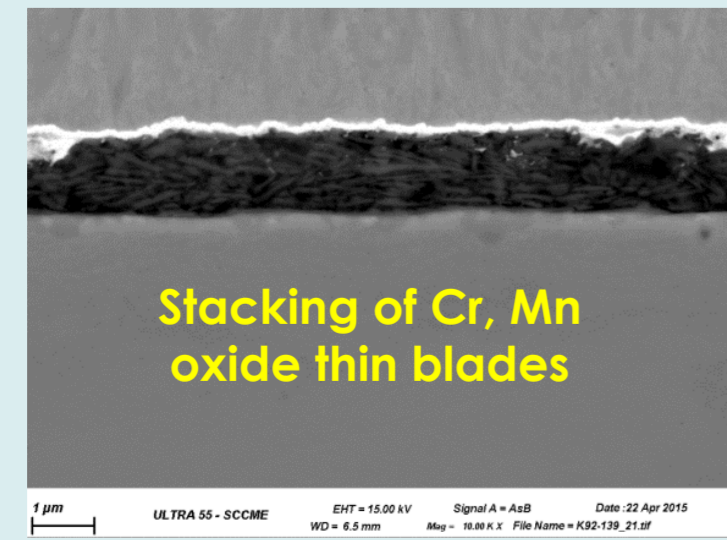
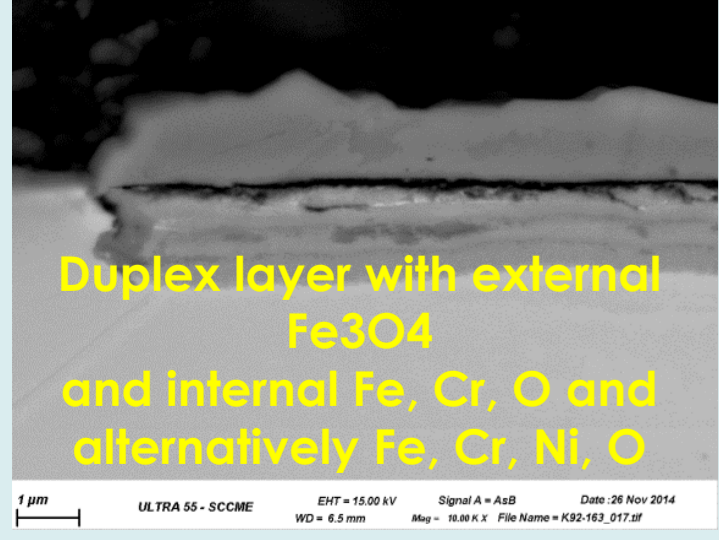
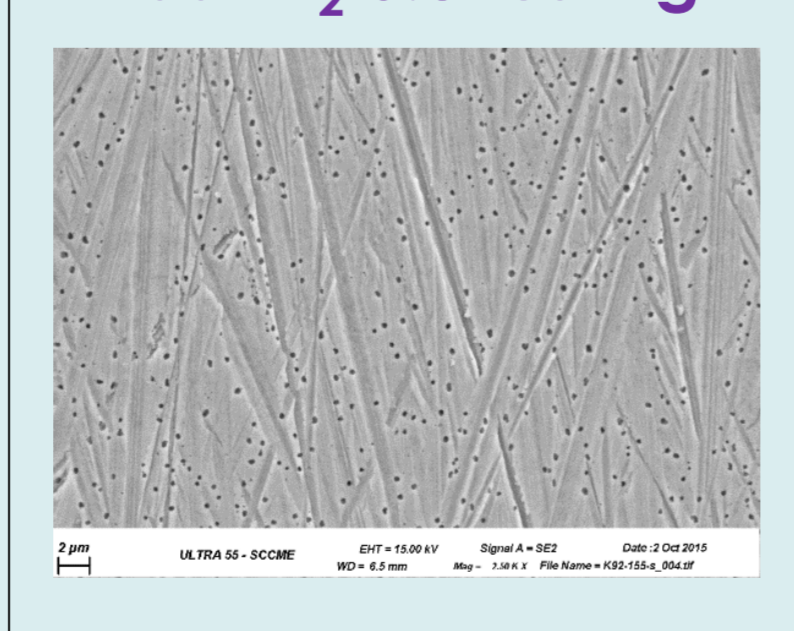
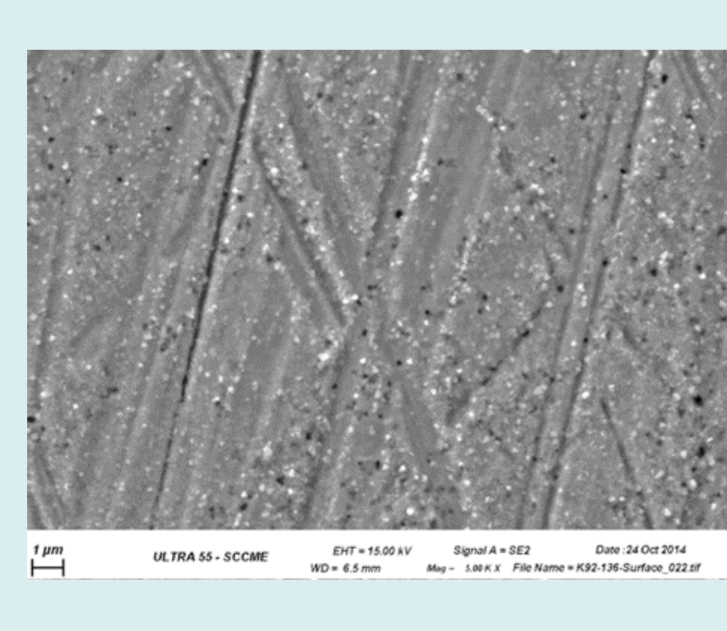
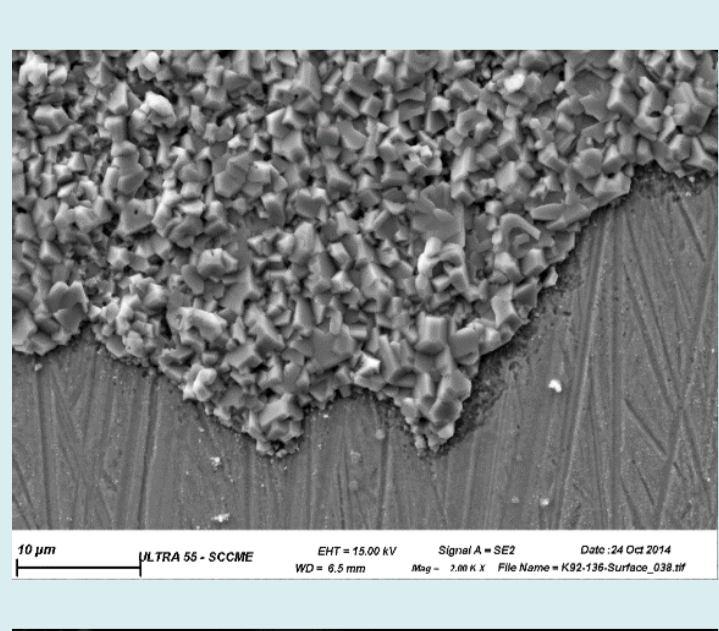
STATIC CONDITIONS

DYNAMIC CONDITIONS

Less low kinetic

Low kinetic

1bar N₂ 6.0 testing



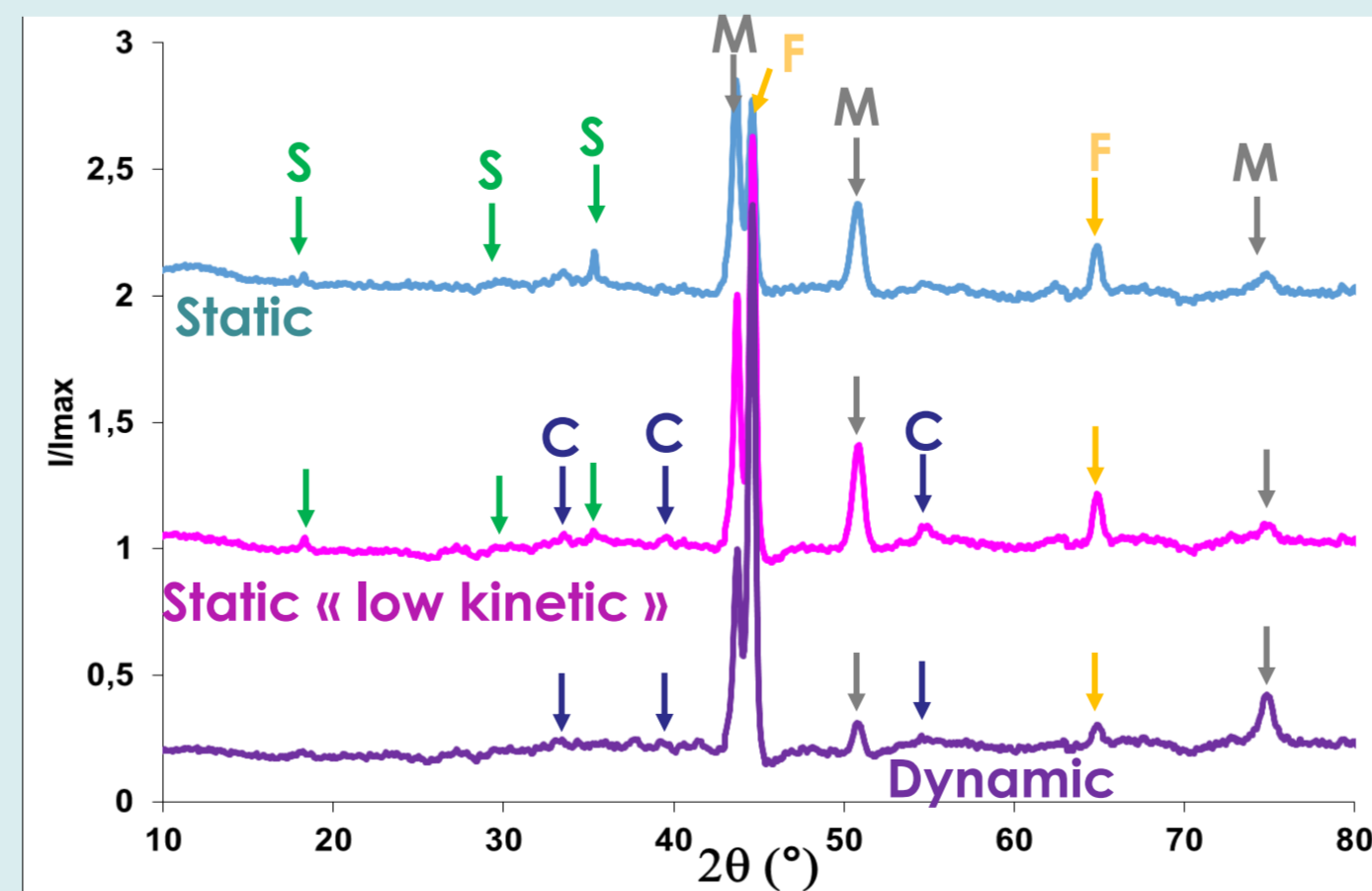
1000 h in 4 cycles of 100+200+200+500 hours

1 cycle of 1000h

- After static under pressure tests, surfaces are heterogeneous : nanometric films and micrometric layers (with different morphology depending on the number of cycles). They are homogeneous for all dynamic tests.
- 2 kinds of oxides form on surface during static test : spinel and chromia containing Mn while main chromia in dynamic test.
- In both cases a new c.c phase in underlying metal (with Fe and Mo).

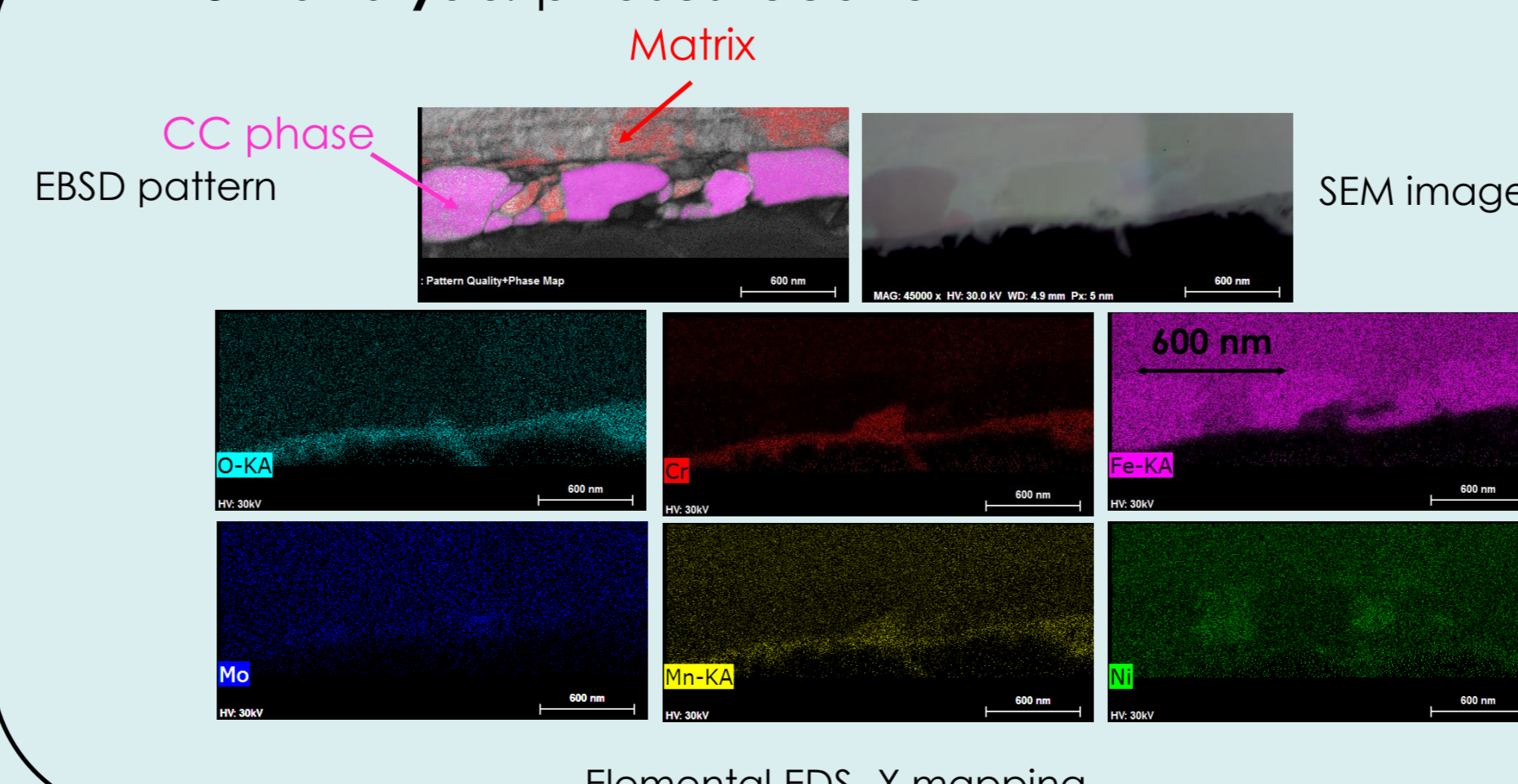
PHASES IDENTIFICATION

- Low incidence angle diffraction (depth analysis ~400 nm using X-ray K α Cu) show **only oxides, no nitrides**.



M : austenitic matrix
F : centered cubic phase
C : (Cr, Mn)₂O₃
S : spinel (CrMn)₃O₄

- EBSD analysis: phases location



Elemental EDS- X mapping

CONCLUSION

Corrosion kinetics of 316 L steel in N₂ environment are low.

Although N has been detected in surface (few 100 nm depth) by GDOES other techniques used reveal no traces of N (even XPS). **Nitridation** risk in ECS conditions can be **eliminated**.

Corrosion phenomena is due to **oxidation** caused by O₂ impurities contained in N₂. Under N₂ flow at 1 bar at 515°C, the oxide film is compact and uniform and seems to be protector (chromia).

In static atmospheres under 180 bar N₂, oxidation behavior depends on the amount and individual duration of cumulative cycles. Fe₃O₄ crystallites formation is associated with increasing corrosion kinetics but those crystallites change with long period cycles.

PROSPECTS

In **static conditions**, gas content is gradually O₂ depleted and the consequences of this depletion will be studied to understand mechanisms in **non-stationary environment**.