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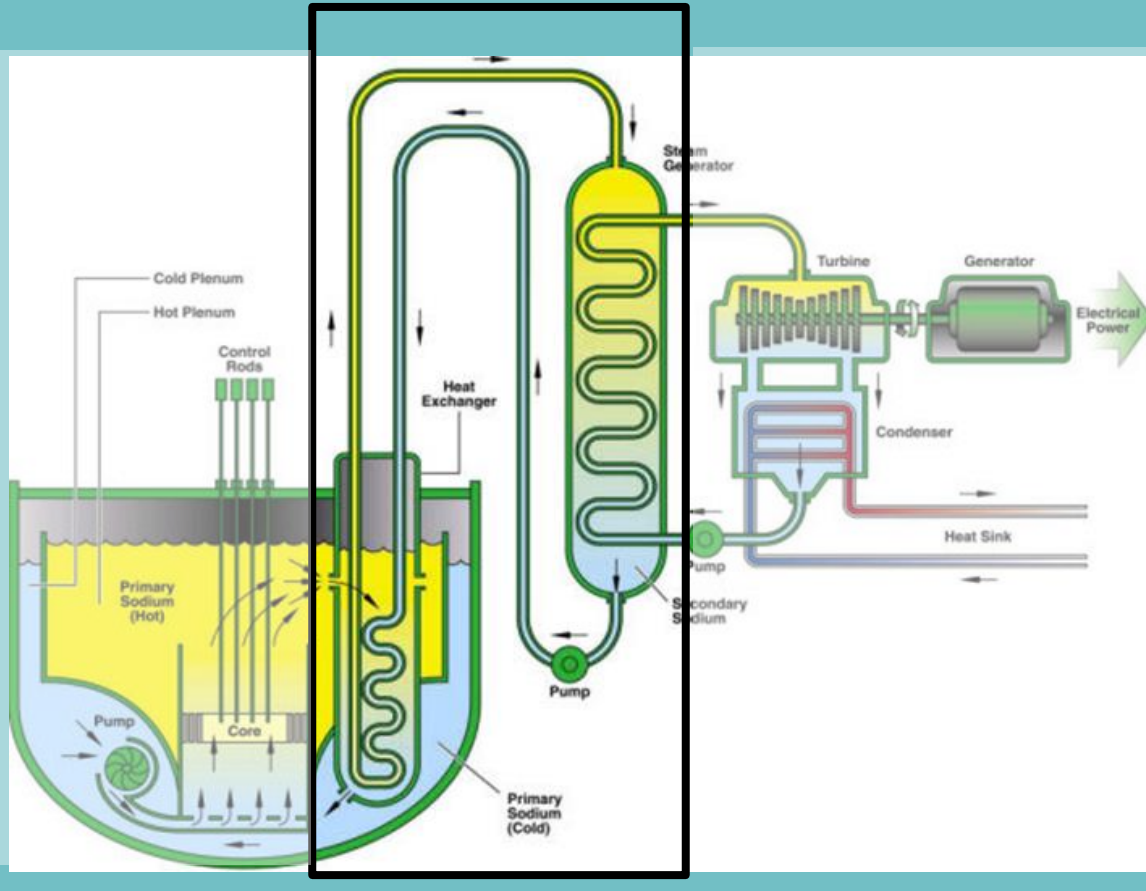
# Corrosion Behavior of a AISI-316 Stainless Steel Grade Type in Nitrogen Environment for a Sodium Gas Heat Exchanger

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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 3<sup>rd</sup> circuit containing **Nitrogen** and maintained at 180 bar to make the turbine rotate.

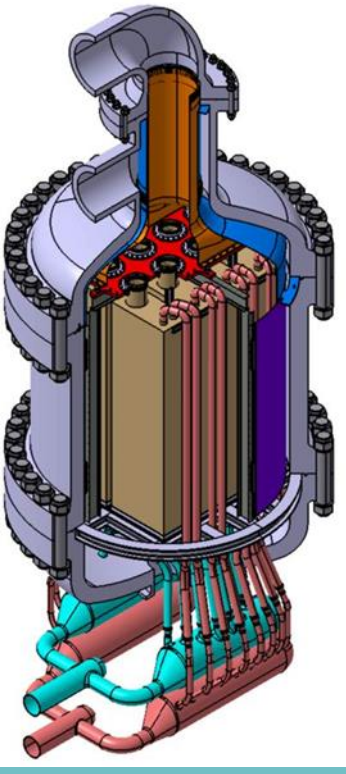
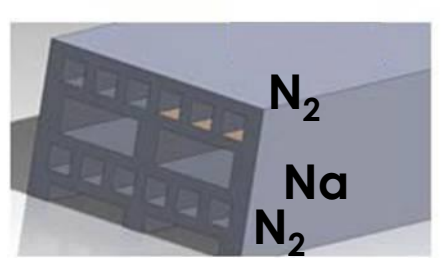
In **Sodium-Gas-Energy Conversion System**, heat transfer takes place inside modulus comprising 2 channels networks: one for nitrogen and the other one with larger section for sodium flowing. Each channels are separated by a wall of 2 mm thick for good thermal conductivity.

Selected material : AISI- 316 SS grade

Working conditions in the modulus:

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

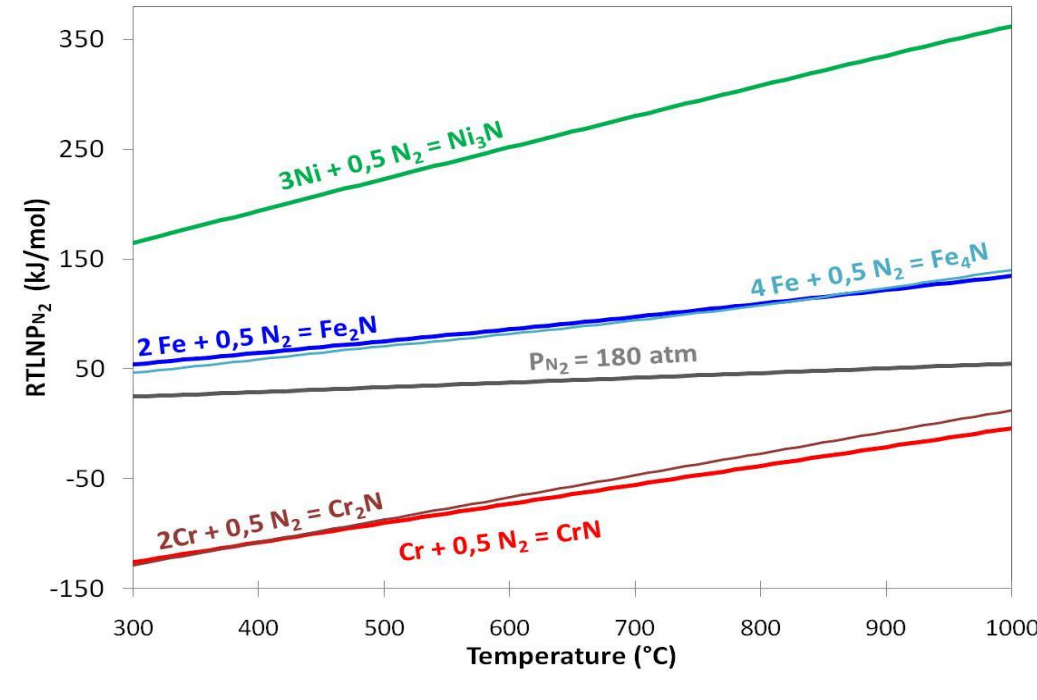
N<sub>2</sub>: P=180 bar ; Inlet  $\theta=315^{\circ}\text{C}$  and Outlet  $\theta=515^{\circ}\text{C}$



## OBJECTIVES

Good performance of the ECS has to be guaranteed for **30 years** → Compatibility of the 316L with N<sub>2</sub> environment at 515°C and 180 bar has to be checked.

Stability of main nitrides as a function of P<sub>N<sub>2</sub></sub>. Activity values of Fe, Cr, and Ni are the molar fraction in 316L. At 515°C and 180 bar N<sub>2</sub>, CrN and Cr<sub>2</sub>N are potentially formed.



Main nitrides Ellingham diagram  
Thermodynamic data from HSC database.

→ Expected phenomenon :

• Nitrogen diffusion onto the surface

→ **nitriding layers**;

• No continuous layer

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

Severity of damages depends on affected thickness.

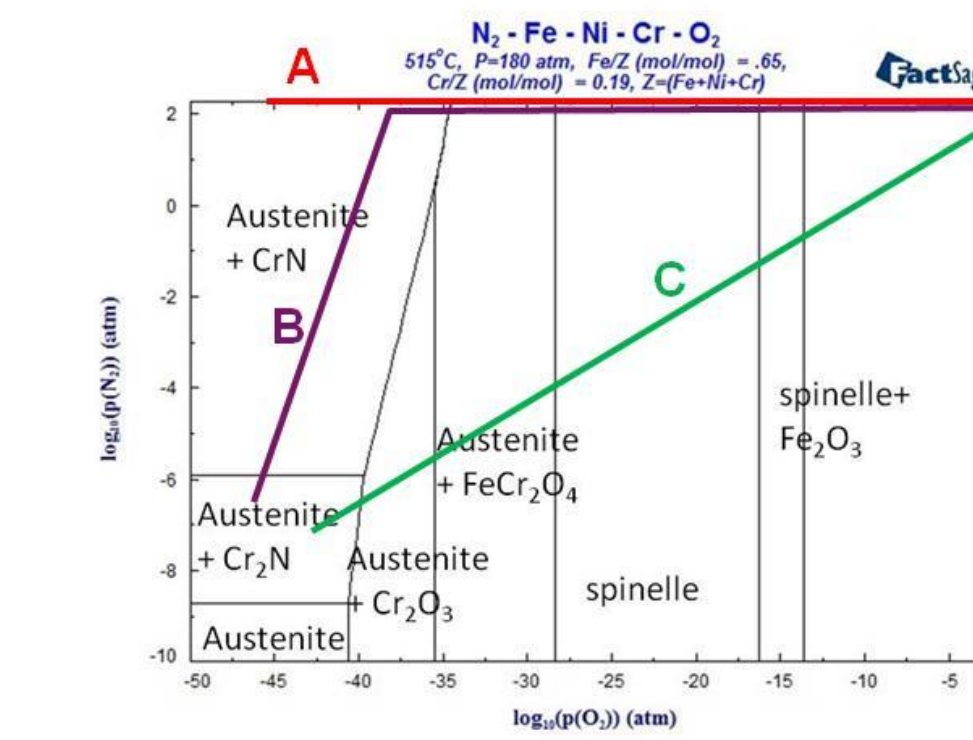
→ Few relevant data within the ECS conditions :

they concern other environment than pure N<sub>2</sub> (NH<sub>3</sub>, N<sub>2</sub>/air or complex atmospheres), other materials (Ni-based alloys) and higher temperature.

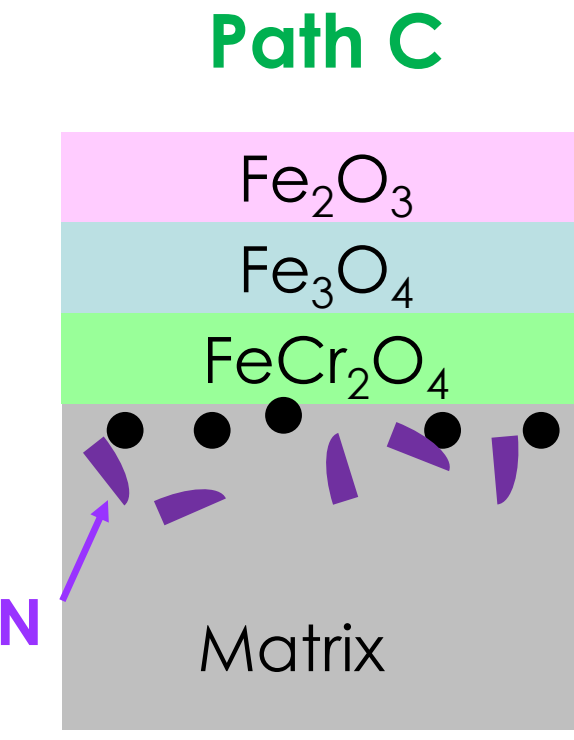
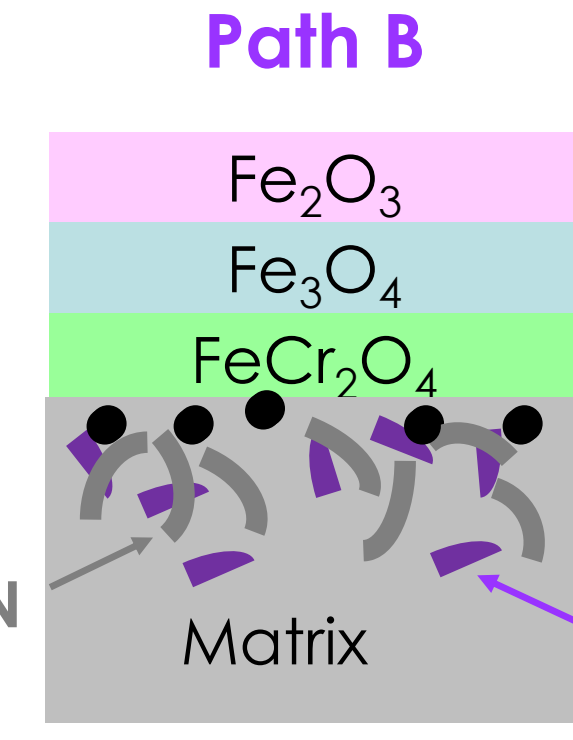
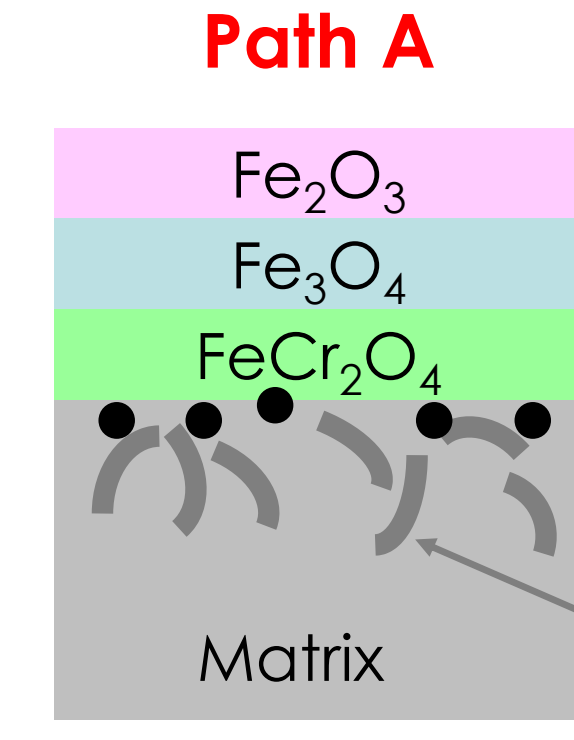
If oxygen is present, competition between nitridation and oxidation may occur.

**Oxidation susceptibility** to take into account.

Considering that both P<sub>N<sub>2</sub></sub> and P<sub>O<sub>2</sub></sub> 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 FactSage.



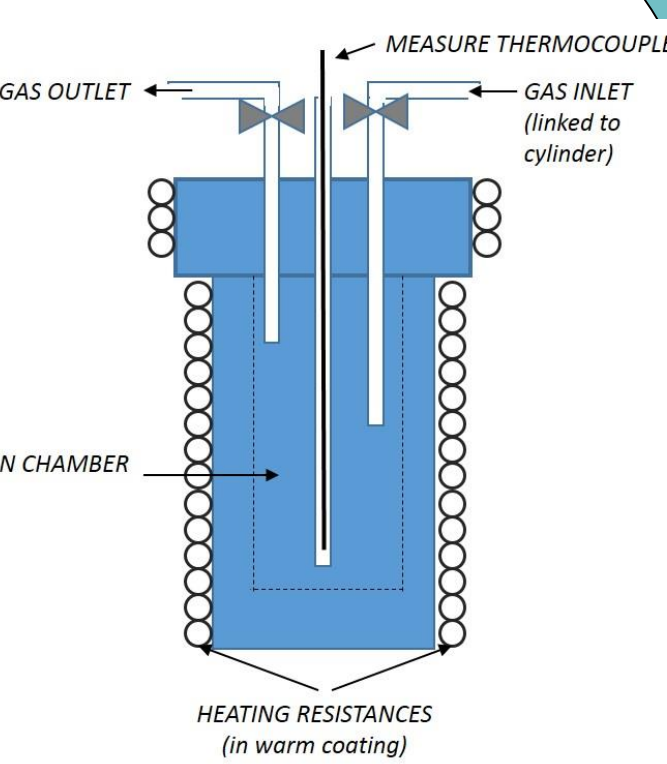
• Cr<sub>2</sub>O<sub>3</sub> internal oxidation

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)

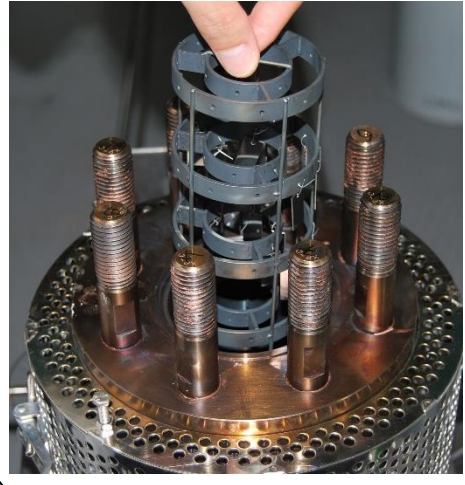
## EXPERIMENTAL

### 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 N<sub>2</sub> (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

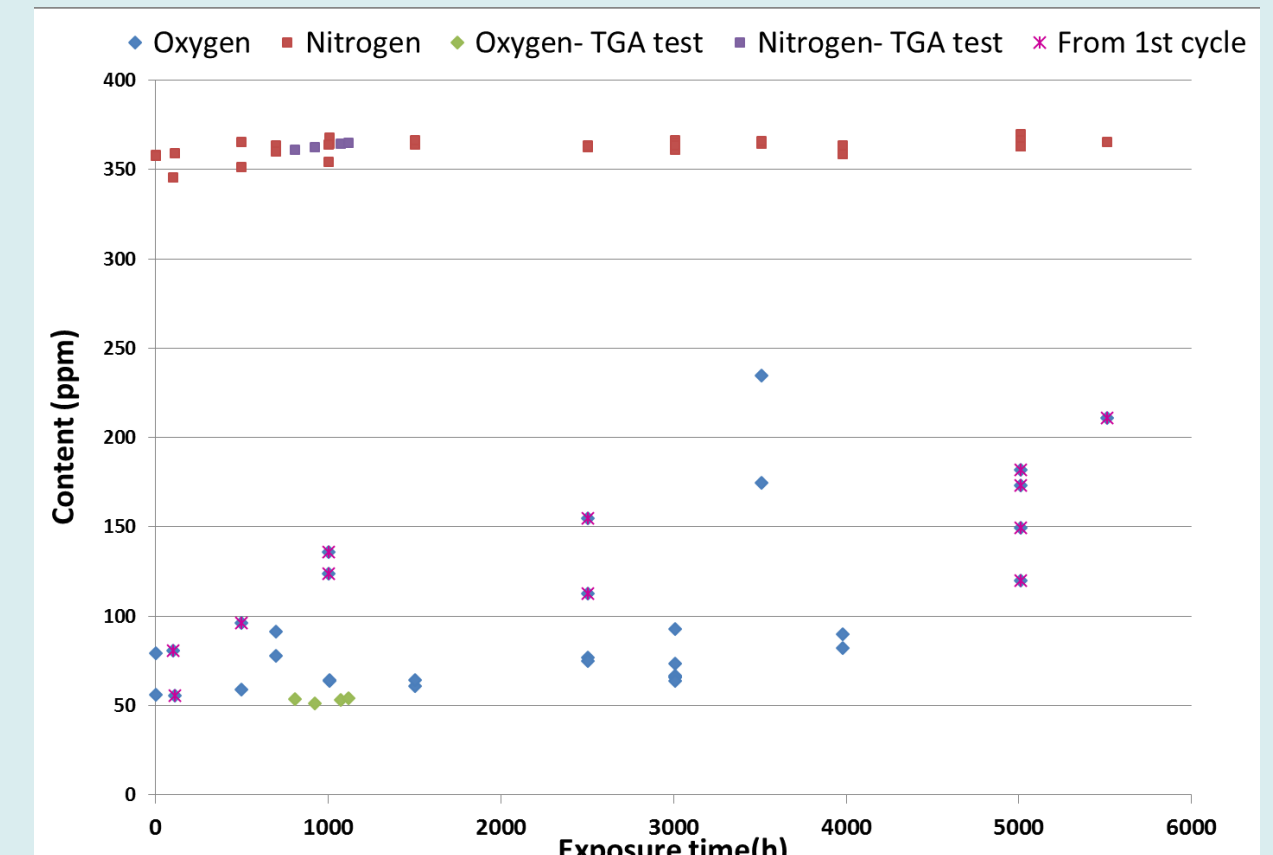
- ❑ Parabolic kinetics in both environment :  $\frac{\Delta m}{S} = \sqrt{k_p t}$ .
- ❑ Static test : 2 well-marked kinetics which depend on introducing time;
- ❑ Dynamic tests : no influence of N<sub>2</sub> purity in range tested;
- ❑ Lowest kinetic obtained in static test = kinetics obtained in dynamic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

### DYNAMIC TEST (P=1 bar)

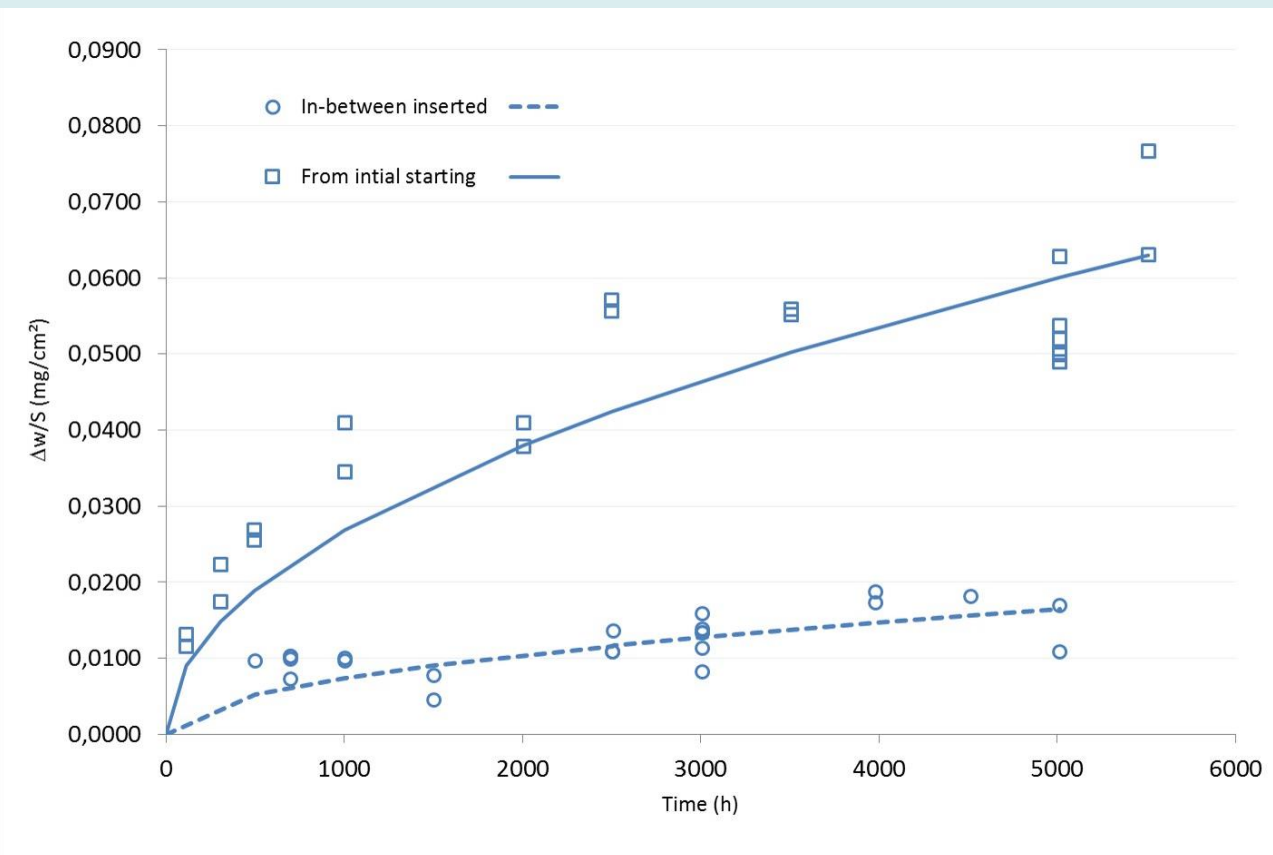
- ❑ In a symmetrical thermogravimetric system (Setaram® TAG24);
- ❑ Gas linear flow rate = 2,2 cm/s at 515°C;
- ❑ 3 qualities of N<sub>2</sub> : with 20 ppm, 3 ppm and 1 ppm of impurities;
- ❑ Continuous mass gain acquisition;
- ❑ PO<sub>2</sub> measured by a zirconia probe mounted at the nearest of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



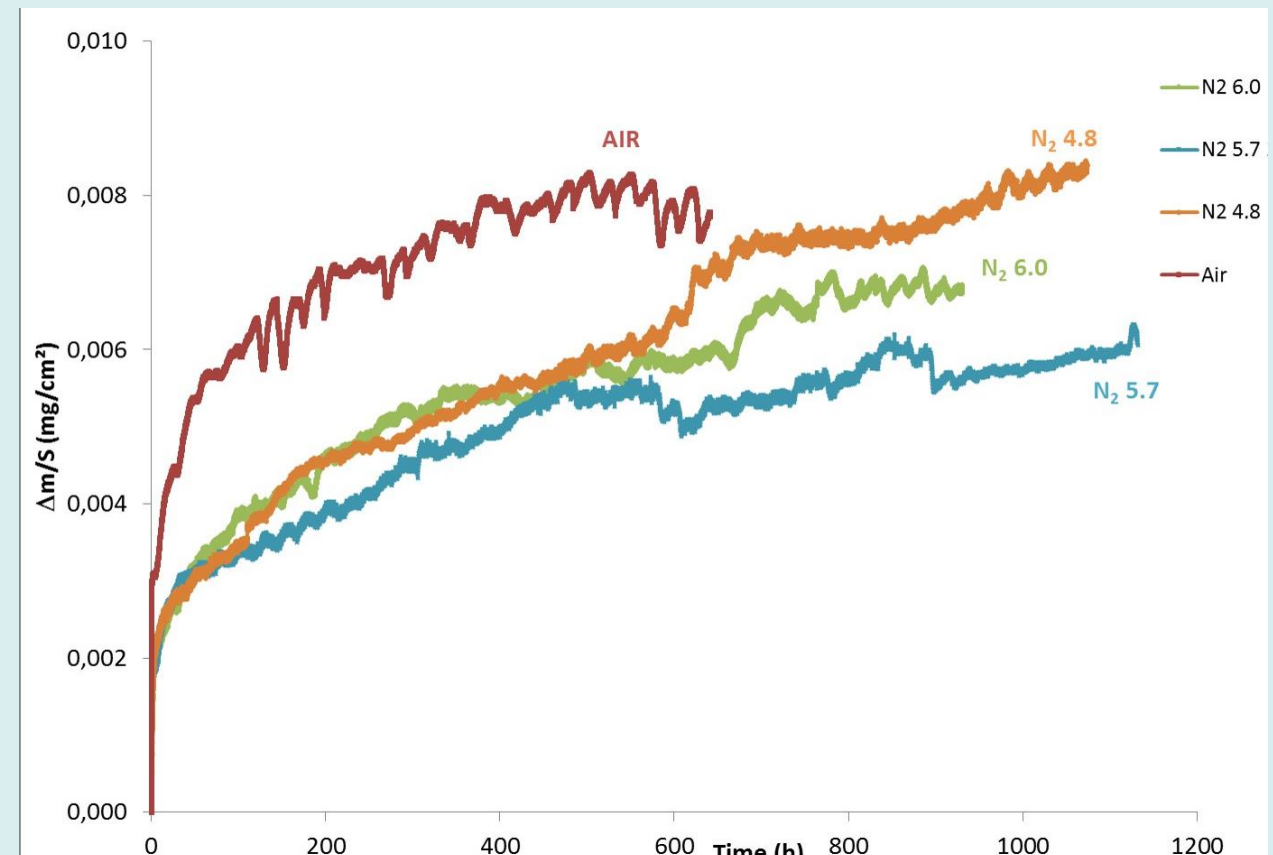
### CHEMICAL ANALYSIS



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



Surfacic weight gain vs exposure time in **static** 180 bar N<sub>2</sub> 4.5 at 515°C

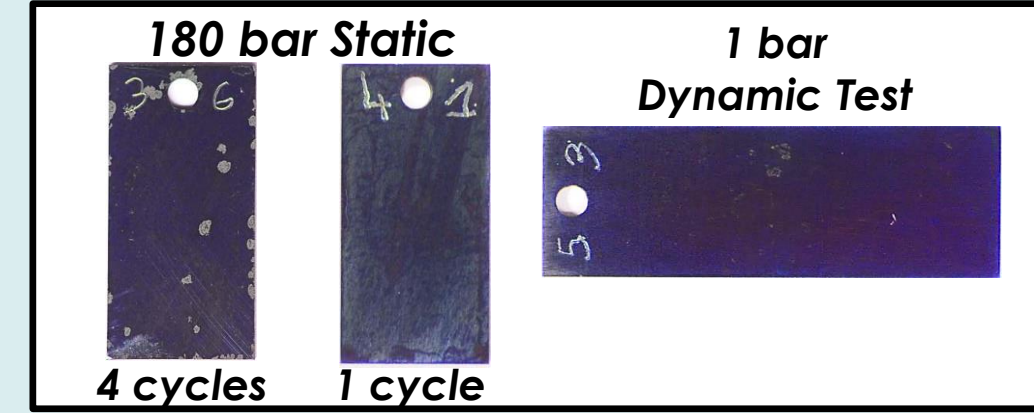


TGA curves at 515°C for different purities of N2

Gas purity	PO <sub>2</sub> (atm)	k <sub>p</sub> (mg <sup>2</sup> .cm <sup>4</sup> .h <sup>-1</sup> )
Dynamic data		
N <sub>2</sub> 4.8	9.10 <sup>-5</sup>	6.1.10 <sup>-8</sup>
N <sub>2</sub> 5.7	2.10 <sup>-6</sup>	2.9.10 <sup>-8</sup>
N <sub>2</sub> 6.0	1.5.10 <sup>-6</sup>	4.7.10 <sup>-8</sup>
Air	0,20	9,2. 10 <sup>-8</sup>
Static data		
N <sub>2</sub> 4.8	3.10 <sup>-4</sup> *	5,4.10 <sup>-8</sup>
		7,2.10 <sup>-7</sup>

\* 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.

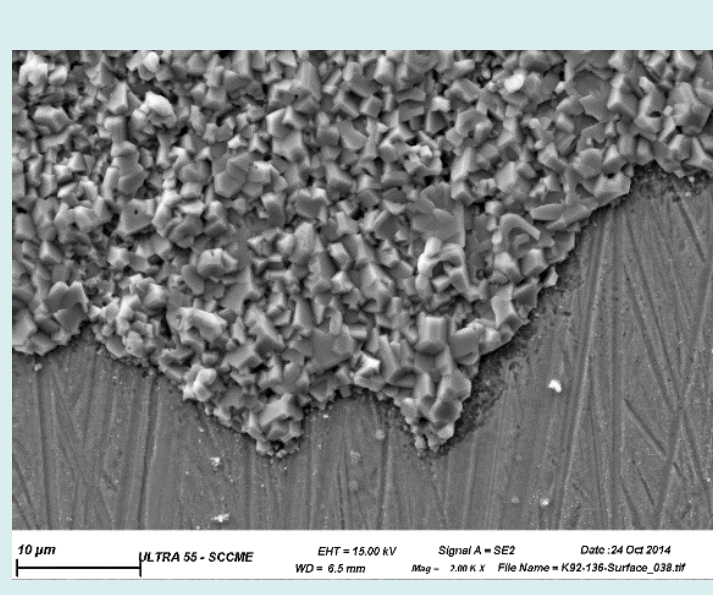
### SURFACE MICROSTRUCTURES

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

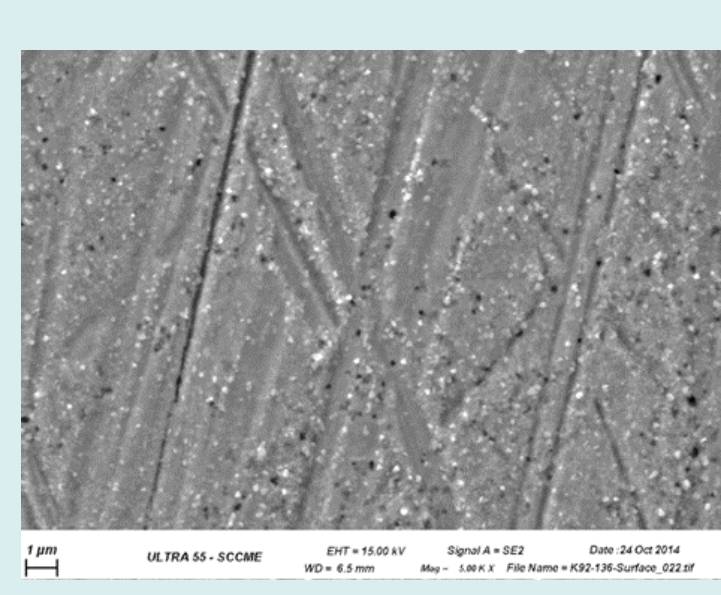
#### STATIC CONDITIONS

#### DYNAMIC CONDITIONS

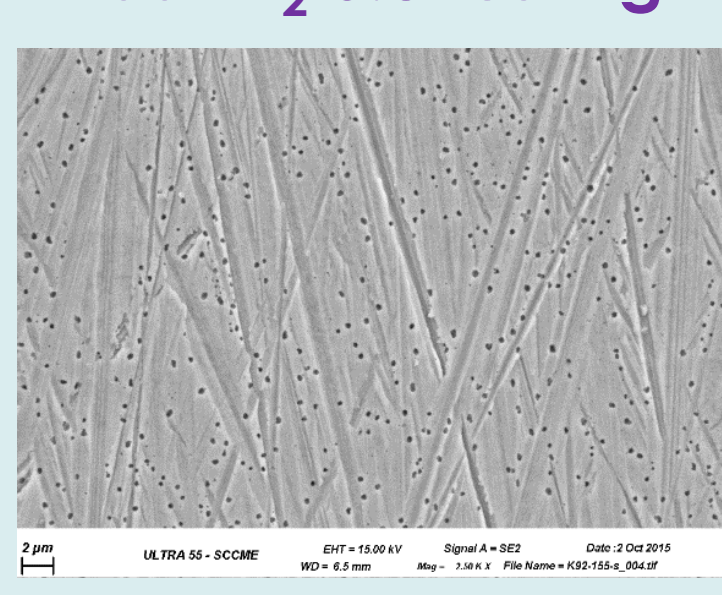
Less low kinetic



Low kinetic



1bar N2 6.0 testing



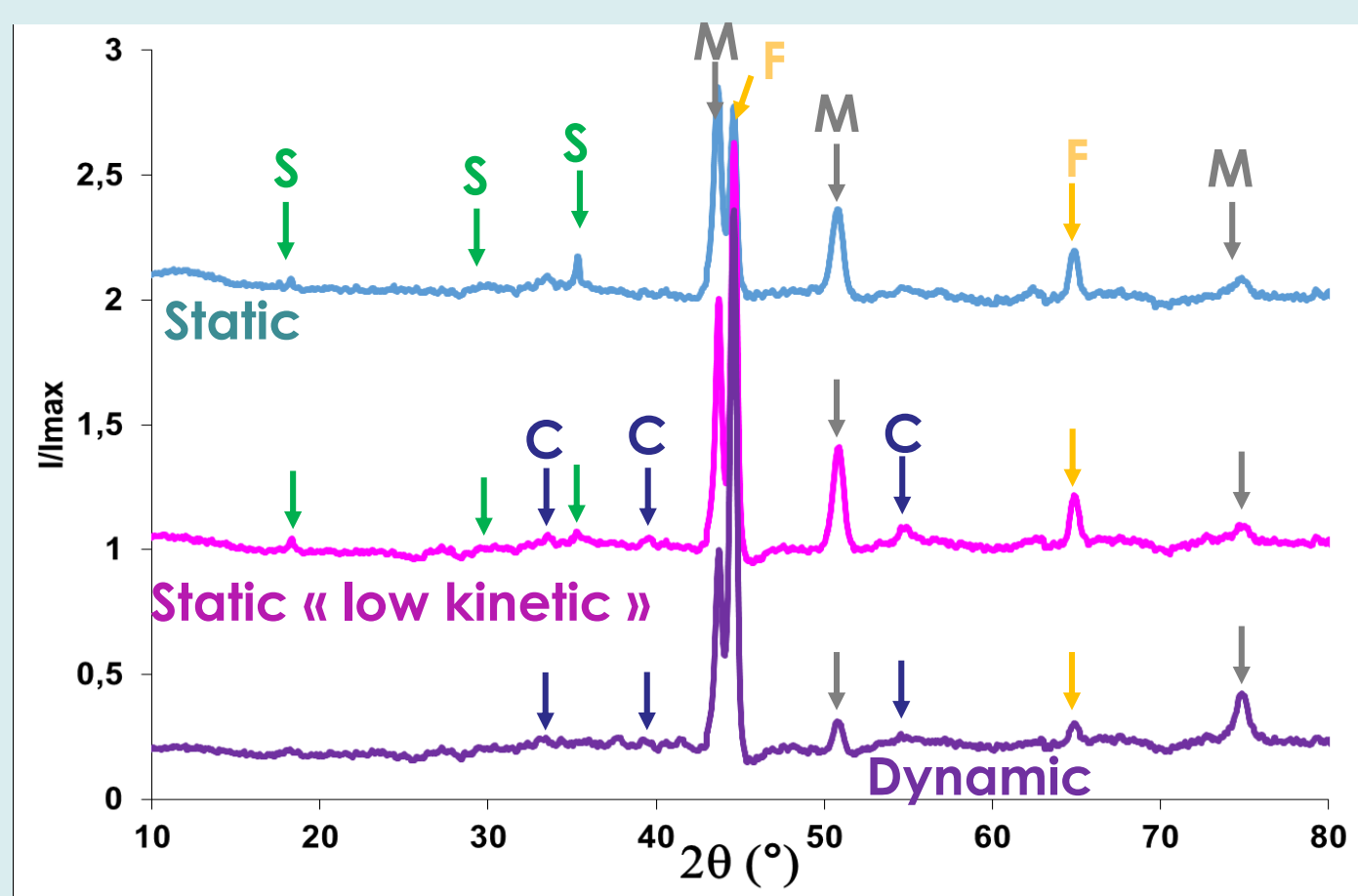
1000 h in 4 cycles of 100+200+200+500 hours

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).

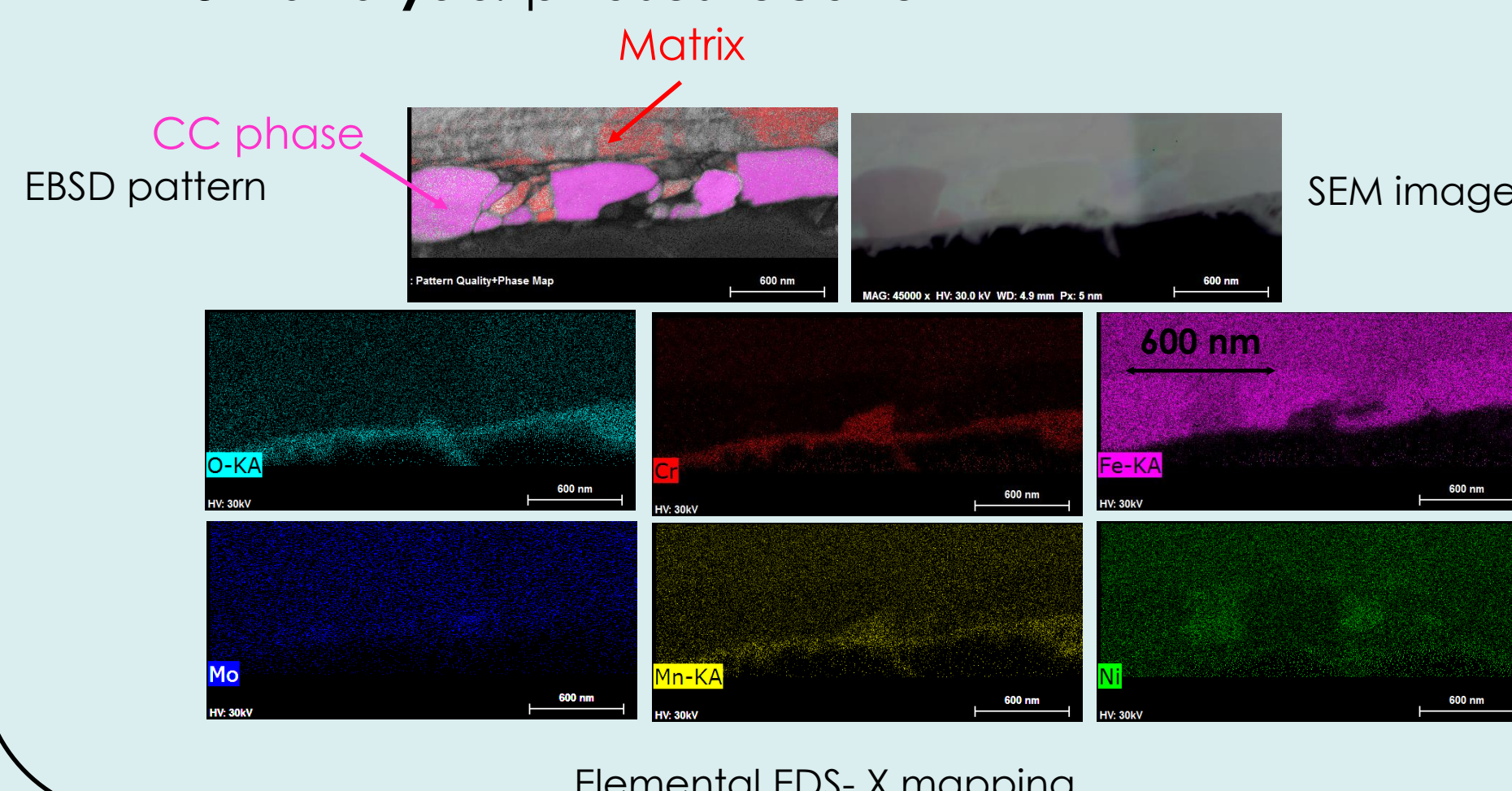
### PHASES IDENTIFICATION

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



M : austenitic matrix  
F: centered cubic phase  
C: (Cr, Mn)<sub>2</sub>O<sub>3</sub>  
S: spinel (CrMn)<sub>3</sub>O<sub>4</sub>

- ❑ **EBSD analysis**: phases location



## CONCLUSION

Corrosion kinetics of 316 L steel in N<sub>2</sub> 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 O<sub>2</sub> impurities contained in N<sub>2</sub>. Under N<sub>2</sub> 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 N<sub>2</sub>, oxidation behavior depends on the amount and individual duration of cumulative cycles. Fe<sub>3</sub>O<sub>4</sub> crystallites formation is associated with increasing corrosion kinetics but those crystallites change with long period cycles.

## PROSPECTS

In **static conditions**, gas content is gradually O<sub>2</sub> depleted and the consequences of this depletion will be studied to understand mechanisms in **non-stationary environment**.