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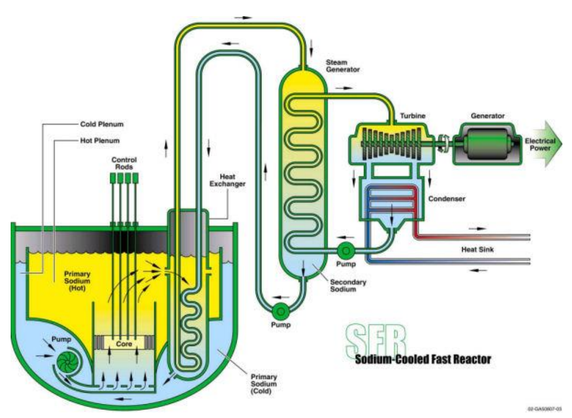
Context and objectives

Austenitic stainless steel 316L(N) (Fe, 18 wt.% Cr, 12 wt.% Ni, 2.3 wt.% Mo, 1.7 wt.% Mn) is the reference material for studied 4th nuclear reactor material sustainability.

Any interactions between the liquid metal and the structural materials must be well known, well understood and predicted to guarantee a 60 years service life-time as well as a good resistance to incidental conditions.

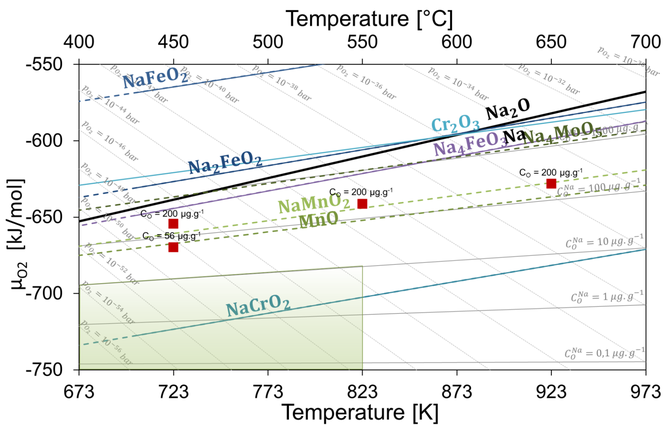
The most important and prevalent impurity in liquid sodium is **oxygen**. With temperature, oxygen is known to be one of the main corrosion parameters in liquid sodium. In fact, the empirical laws proposed for the **dissolution** of austenitic steel in liquid sodium mainly depend on the oxygen content. Moreover, thermodynamics data point out that **oxidation** might occur, with the formation of **sodium chromite** ($NaCrO_2$). Oxidation is observed on 316L(N) stainless steel exposed to static liquid sodium and parts of Phénix Sodium Fast Reactor.

The objectives of the study are to understand oxygen-enhanced corrosion, to identify implied mechanisms and to model them in order to improve the long-term prediction.



4th nuclear reactor cooled by liquid sodium

Thermochemistry



Ellingham diagram of Na_2O-M_xO_y-type oxides

- Investigated points
- Operating conditions in nuclear reactors

This study
Possible sodium chromite formation
Oxidizing conditions
Oxygen effects on dissolution

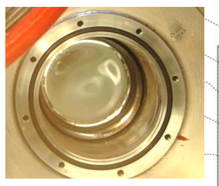
Industrial operating conditions
Possible Sodium chromite formation

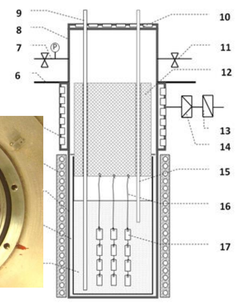
Corrosion testing

- Static liquid sodium (CORRONa)

- Chemistry sodium control
  - Purification (oxygen hot trapping by Zr foil)
  - Oxygen adding (bubbling or Na_2O): 56 or 200 µg.g^{-1}
  - Using of oxygen tracer (^{16}O then ^{18}O)

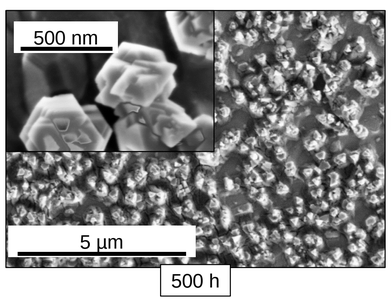
- Temperature: 450 °C, 550 °C or 650 °C
- Duration: 100 h to 5000h





Results at 550°C, C_O=200 µg.g^{-1}

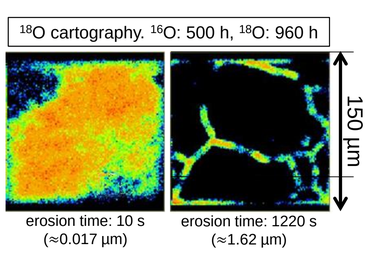
Surface characterizations



XRD: Mo_3Fe_3C, $NaCrO_2$ (?)
SEM: Crystals (Na, Cr, O)

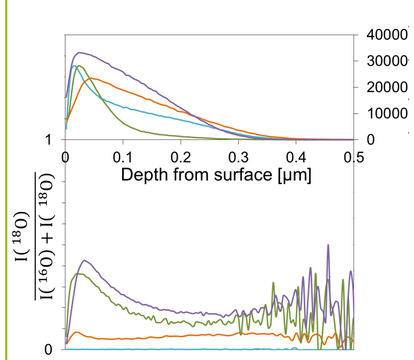
$NaCrO_2$ formation: Carburization

Oxygen tracer test (SIMS characterization)

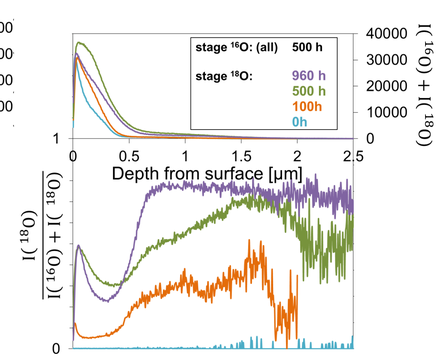


^{18}O: materials enriched with time, especially inside the grain boundaries

$NaCrO_2$ formation: Oxide/alloy interface Grain boundaries

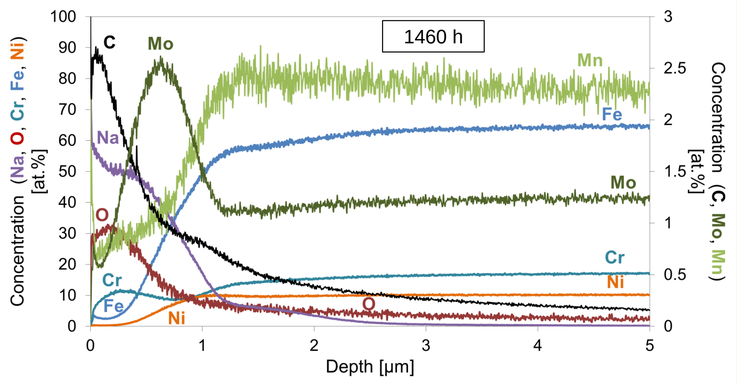


Profile above a grain



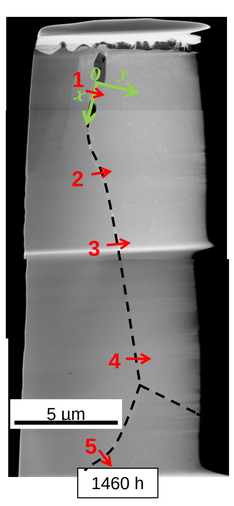
Profile on grain boundary

Chemical profiles: GDOES characterizations



1st layer: rich in Cr, Na, O and C
2nd layer: rich in Mo and C
Then: Cr-depleted zone

Local diffusion: STEM-EDX

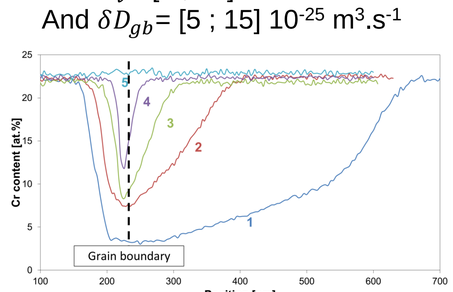


Cr concentration gradient along and around a grain boundary

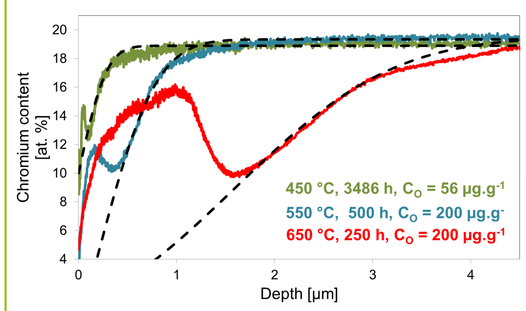
$$c(x,y,t) = c_0 \cdot \exp\left(-\frac{1}{\pi^{1/4}} \cdot \frac{\eta}{\beta^{1/2}}\right) \cdot \left(1 - \operatorname{erf}\frac{y}{2\sqrt{D_v t}}\right)$$

$$\beta = \frac{\delta D_{gb}}{2 D_v \sqrt{D_v t}} \text{ and } \eta = \frac{x}{\sqrt{D_v t}}$$

➔ D_v= [2 ; 20] 10^{-23} m².s^{-1}
And δD_{gb}= [5 ; 15] 10^{-25} m³.s^{-1}



All conditions

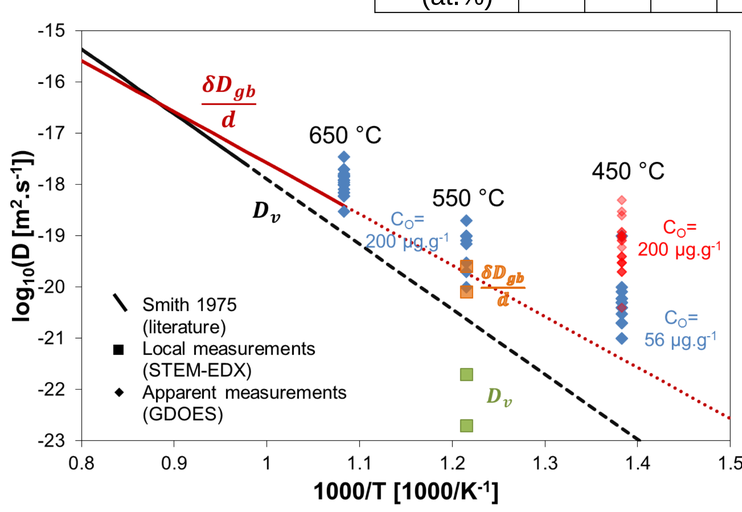


Chromium profile fitting:

$$\frac{C_{Cr} - C_{surf}}{C_{init} - C_{surf}} = \operatorname{erf}\frac{x}{2\sqrt{D_{app} t}}$$

➔ D_{app} and C_{surf}

T [°C]	450	450	550	650
C_O (µg.g^{-1})	56	200	200	200
$\langle C_{surf} \rangle$ (at.%)	6.4	4.7	3.3	10



Local diffusion coefficient:
- good agreement for grain boundaries
- Volume diffusion coefficient lower than the one found in the literature

Apparent diffusion coefficient:
- Good agreement for low sodium oxide activity
- Higher chromium flux for high oxygen activity (450°C, C_O=200µg.g^{-1}) ➔ other corrosion phenomenon?

Conclusion and prospect

Several phenomena are identified: dissolution, oxidation and carburization
Some mechanisms are specifically studied:
- Reaction interface
- Chromium diffusion

The chromium profile seems to be explained by diffusion mechanisms:
The effect of grain boundaries is observed and agrees well
with the published local diffusion coefficient as well as the apparent diffusion coefficient agrees well with the values found in the literature

Other phenomena can be extensively studied:
Carburization by liquid sodium
and
Dissolution

Thermodynamics data predict iron dissolution enhancement with oxygen content and may explain the behaviour at 450°C, where chromium diffuses inside the alloy more quickly when the liquid sodium contains 200 µg.g^{-1} of oxygen content than when it contains 56 µg.g^{-1} of oxygen content

Acknowledgements

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