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OXIDATION OF 316L(N) STAINLESS STEEL IN LIQUID SODIUM AT 550°C

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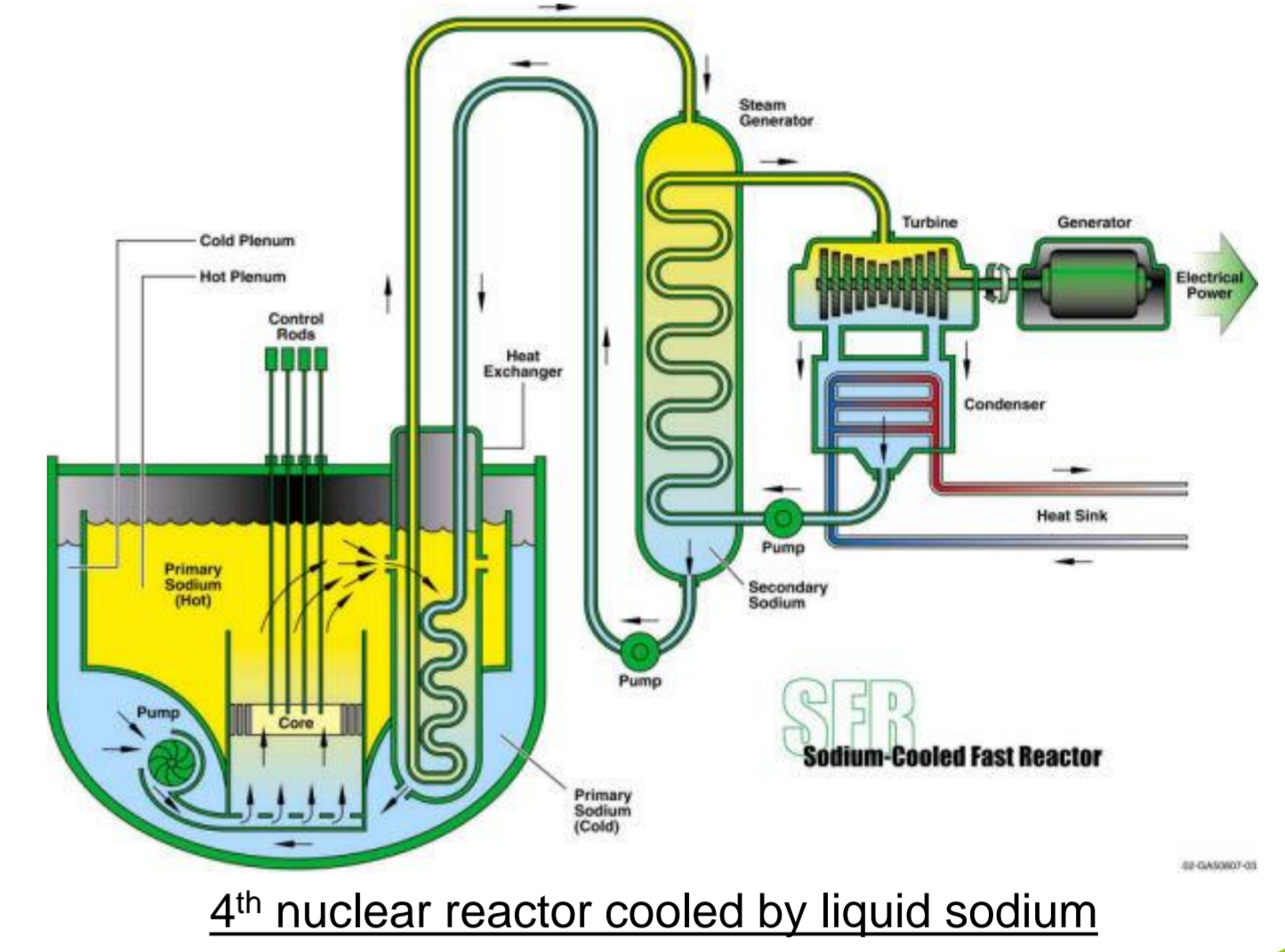
Context and objectives

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.

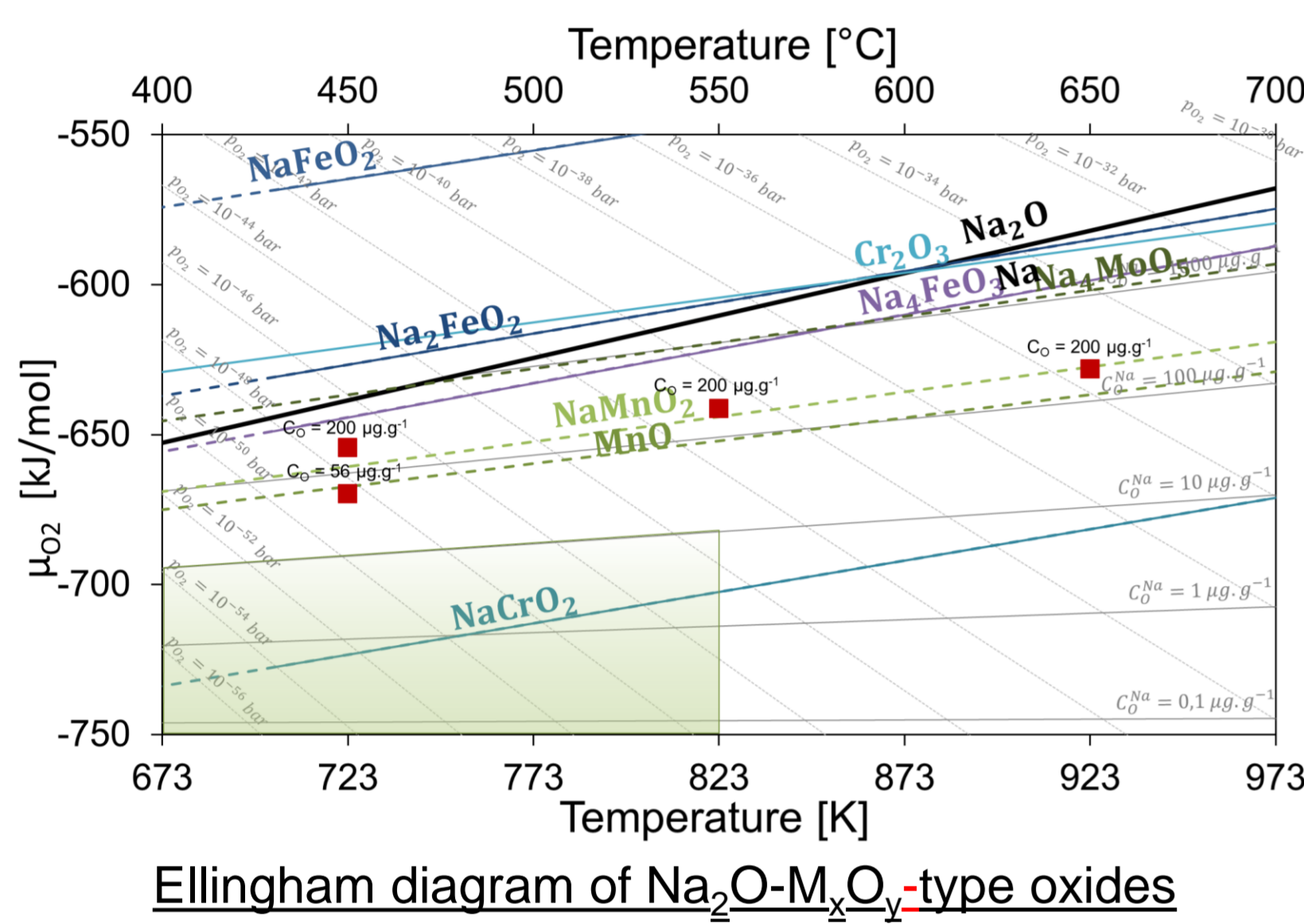
Any interactions between the liquid metal and the structural materials must be well known, well understood and predicted to guarantee a 60 years service life-time as well as a good resistance to incidental conditions.

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** (NaCrO₂). 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.



Thermochemistry



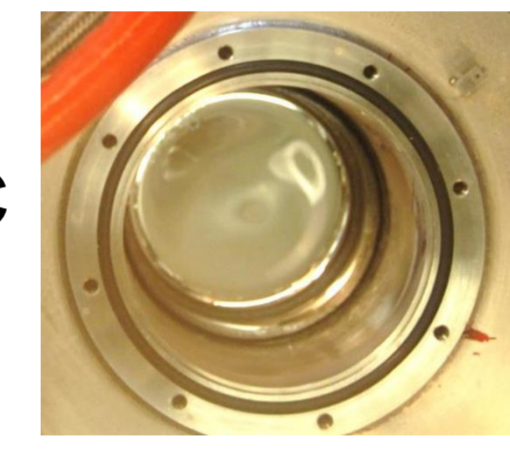
■ Investigated points
 ■ Operating conditions in nuclear reactors

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

Industrial operating conditions
 Possible Sodium chromite formation

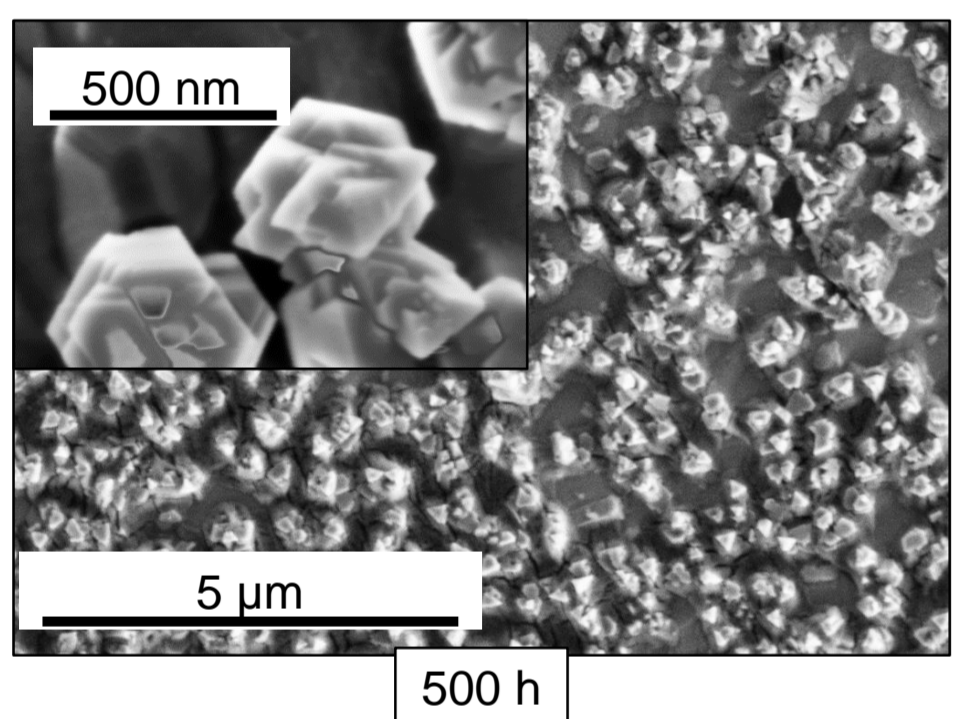
Corrosion testing

- Static liquid sodium (CORRONa)
- Chemistry sodium control
 - Purification (oxygen hot trapping by Zr foil)
 - Oxygen adding (bubbling or Na₂O): 56 or 200 μg.g⁻¹
 - Using of oxygen tracer (¹⁶O then ¹⁸O)
- Temperature: 450 °C, 550 °C or 650 °C
- Duration: 100 h to 5000h



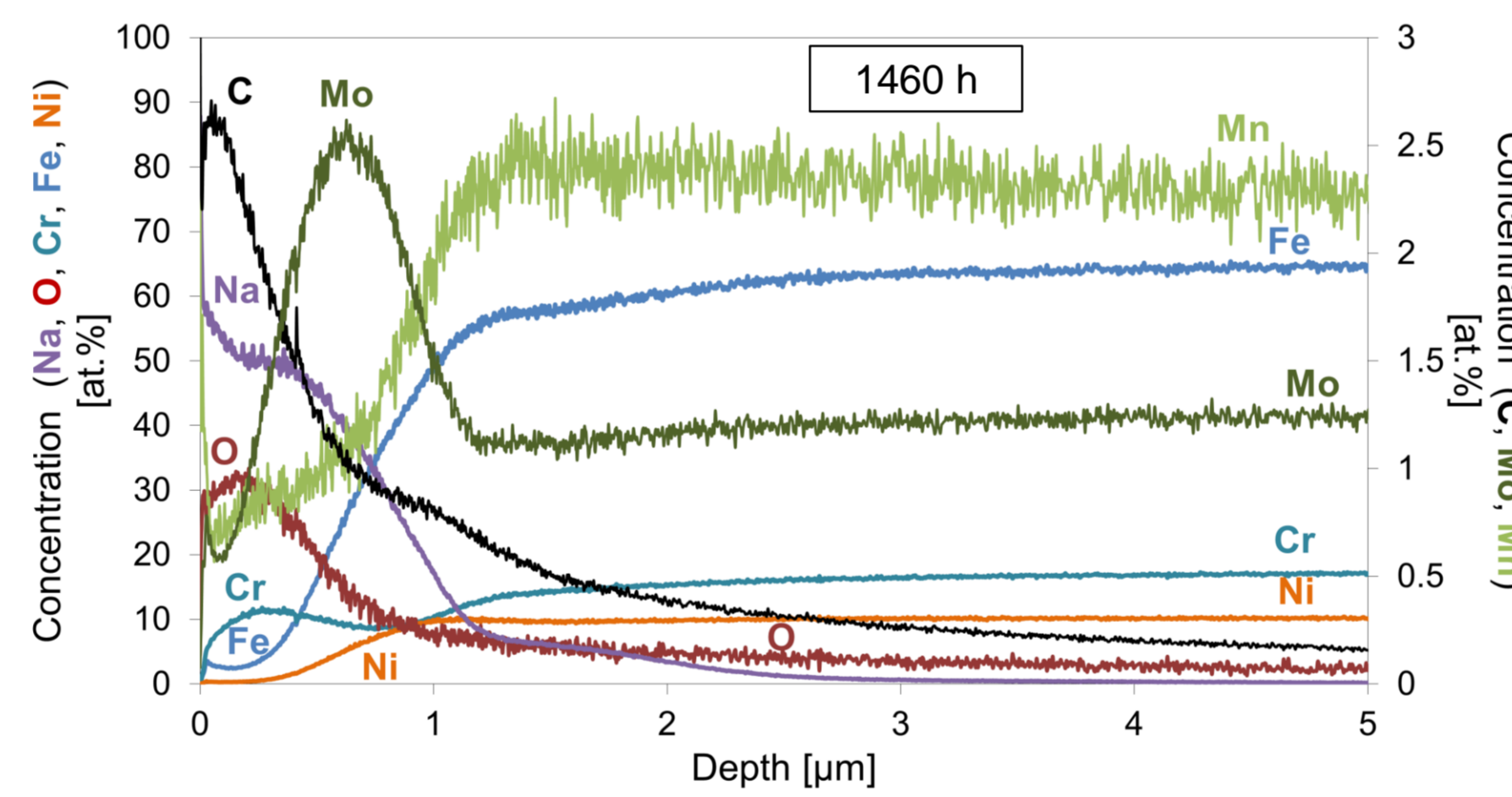
Results at 550°C, C_O=200 μg.g⁻¹

Surface characterizations



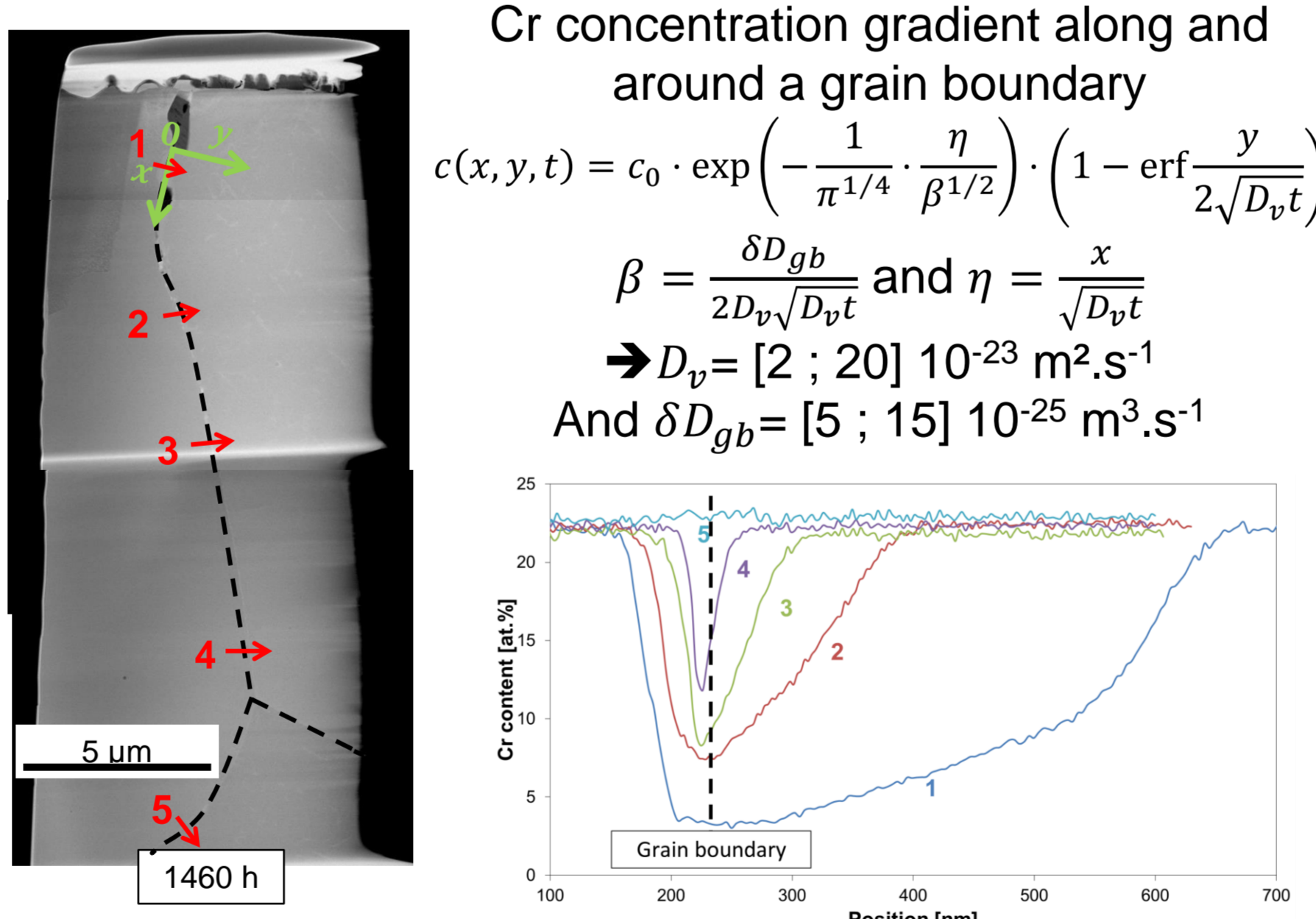
XRD: Mo₃Fe₃C
 NaCrO₂ (?)
 SEM: Crystals (Na, Cr, O)
 NaCrO₂ formation: Carburization

Chemical profiles: GDOES characterizations



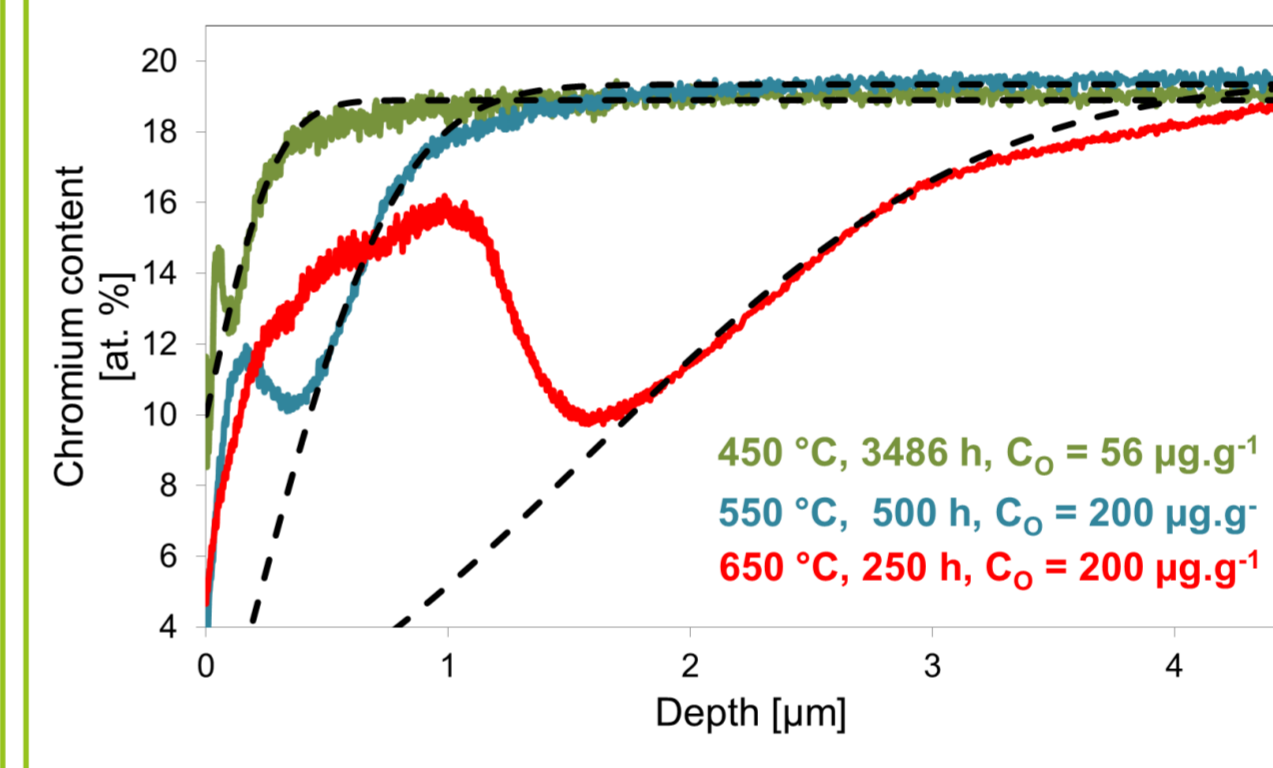
1st layer: rich in Cr, Na, O and C
 2nd layer: rich in Mo and C
 Then: Cr-depleted zone

Local diffusion: STEM-EDX



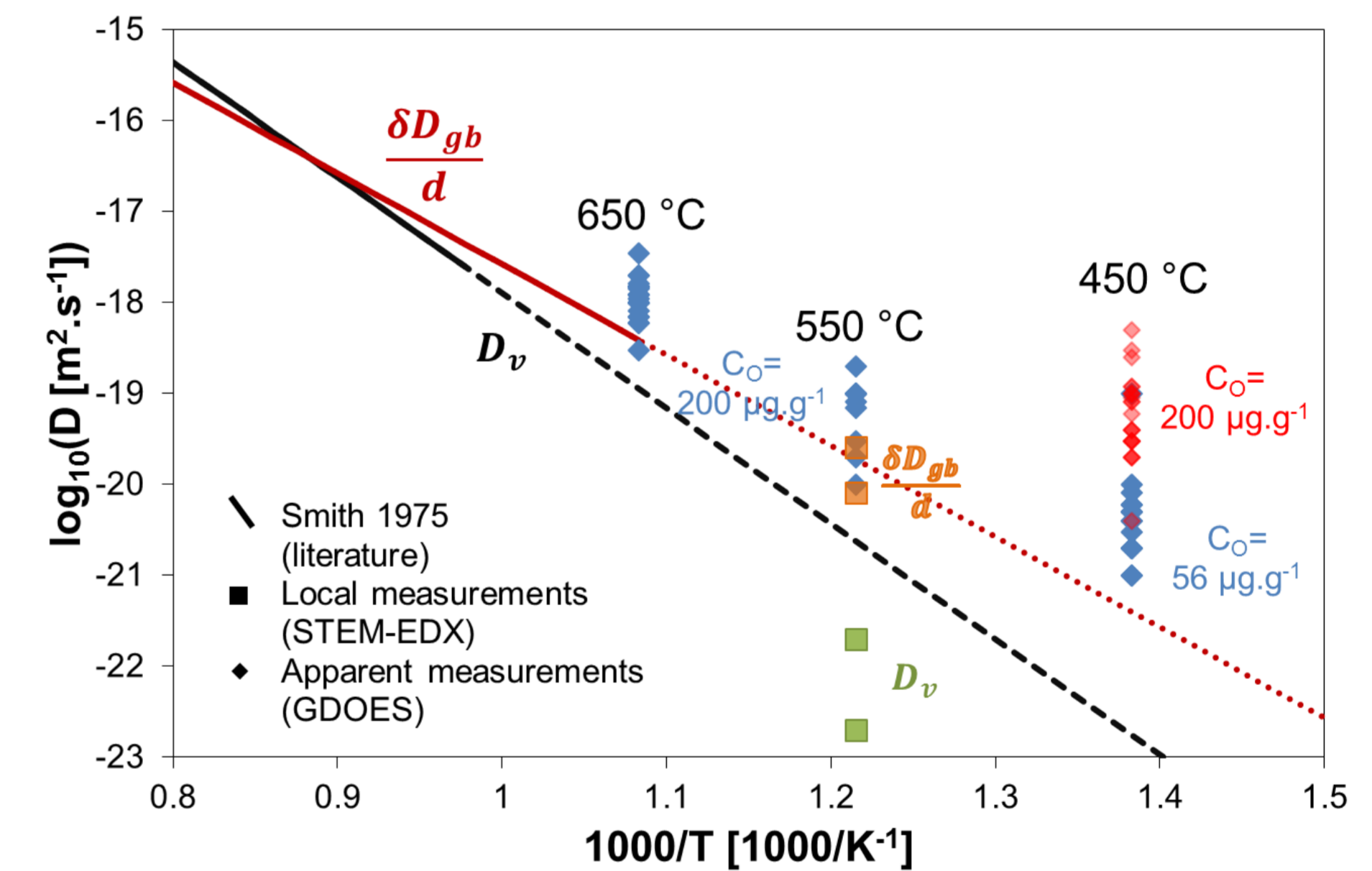
Cr concentration gradient along and around a grain boundary
 $c(x, y, t) = c_0 \cdot \exp\left(-\frac{1}{\pi^{1/4}} \cdot \frac{\eta}{\beta^{1/2}}\right) \cdot \left(1 - \operatorname{erf}\frac{y}{2\sqrt{D_v t}}\right)$
 $\beta = \frac{\delta D_{gb}}{2D_v \sqrt{D_v t}}$ and $\eta = \frac{x}{\sqrt{D_v t}}$
 $\rightarrow D_v = [2 ; 20] \cdot 10^{-23} \text{ m}^2 \cdot \text{s}^{-1}$
 And $\delta D_{gb} = [5 ; 15] \cdot 10^{-25} \text{ m}^3 \cdot \text{s}^{-1}$

All conditions



Chromium profile fitting:
 $\frac{C_{Cr} - C_{surf}}{C_{init} - C_{surf}} = \operatorname{erf}\frac{x}{2\sqrt{D_{app}t}}$
 $\rightarrow D_{app}$ and C_{surf}

T [°C]	450	450	550	650
C _O (μg.g ⁻¹)	56	200	200	200
(C _{surf}) (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

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

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

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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References

Noden *et al.*, *J. of the Brit. Nuc. En.* 12-1 (1973) p.57&p.329
 Shiao *et al.*, *J. of Nuc. Mat.* 67 (1977) p.13
 Bhat *et al.*, *Werkstoffe und Korrosion* 39 (1988) p.115
 Hemery *et al.*, *Corr. Sc.* 76 (2013) p.441
 Hemery *et al.*, *Corr. Sc.* 83 (2014) p.1

Mehrer, *Diffusion in solid* 2007
 Wagner, *J. of the Electroch. Soc.* 99-10 (1952) p.369
 Fisher, *J. of Appl. Phys.* 22-1 (1951) p.74
 Smith, *Met. Sc.* 9 (1975) p.375