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**Microstructure impact on high temperature corrosion
behavior of AISI 316L stainless steel additively
manufactured by Selective Laser Melting (AM-SLM)**

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Abstract

Additive Manufacturing by Selective Laser Melting (AM-SLM) is a near-net shape method producing dense and geometrically complex materials from micrometric powders. This process involves complete melting and very high cooling rates who induce a **refinement** of microstructure, improving the mechanical properties of the material [1,2]. However, the impact of these new microstructures on real functioning properties, like for instance the high temperature durability, needs to be studied. In this purpose, AISI 316L is considered in this work. Samples elaborated by AM-SLM and by conventional metallurgy were oxidized under laboratory air at 900°C for periods up to 3000h. The results highlight better behaviour for AM samples, which present a very good corrosion resistance throughout the 3000 hours. The conventional samples show a good resistance only during the first 1000 hours. These differences were related to the different composition of the oxide layers growing on the surface of the samples during the high temperature ageing: **protective chromia for AM-SLM and non-protective iron oxides for conventional samples**. To explain these differences of reactivity, several hypotheses were considered. XRD, SEM-EBSD and TEM studies were performed on initial samples in order to evaluate their microstructure, surface mechanical state and crystallographic orientation. The most promising hypothesis seems to be related to the microstructure (probably at **nanoscale**) of the samples. For AM-SLM coupons, a typical cellular structure was identified by TEM, with a size between 0.2 and 1 µm, corresponding to a very dense network of dislocations, which accumulate forming cell walls. Dislocation might act during the high temperature exposure as short-circuit paths for Cr diffusion from the bulk to the surface allowing the growth of protective scales for long ageing times. Moreover, AM-SLM samples found to contain large quantity of nano-inclusion that might equally influence corrosion behaviour.

Materials and methods

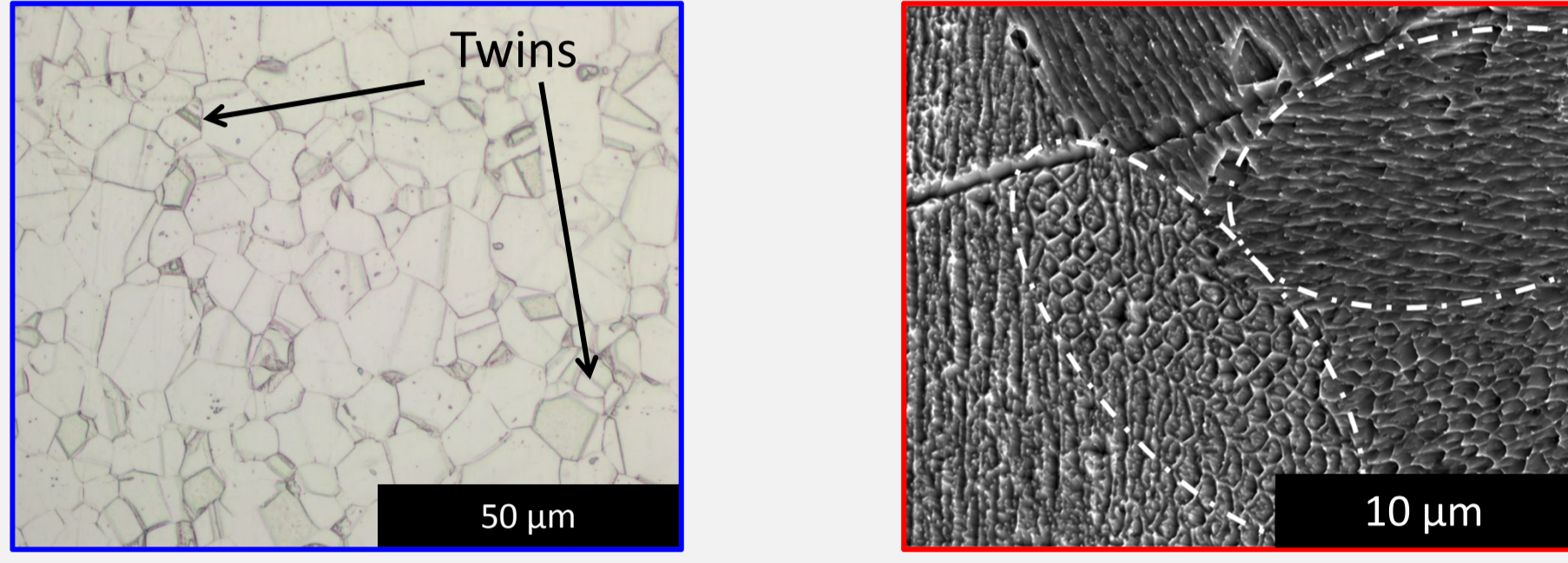
Raw materials

Conventional metallurgy: **Cold-rolling**
Additive Manufacturing: **SLM**

Chemical composition (% weight)

	Cr	Ni	Mo	Mn	Si	C	P	S	Fe
Cold-rolled	17,37	11,03	2,16	1,64	0,56	0,02	0,01	0,002	Bal.
SLM	18,00	12,00	2,30	0,03	0,47	0,01	≤0,04	≤0,005	Bal.

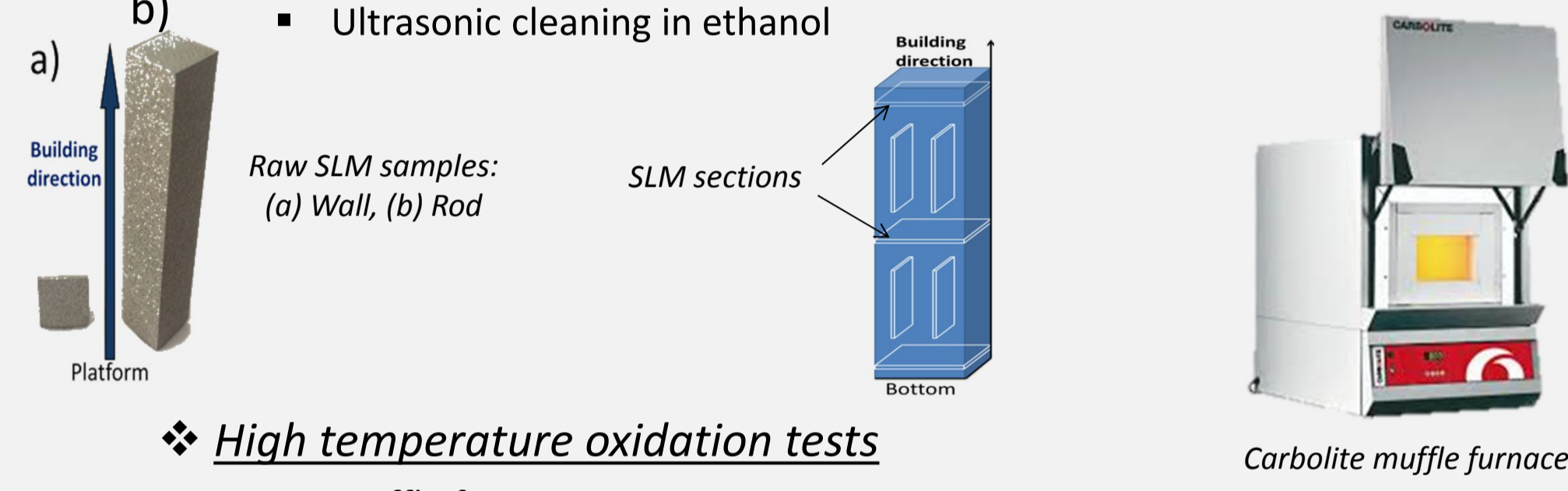
Microstructures of cold-rolled and SLM samples



Experimental

Samples preparation

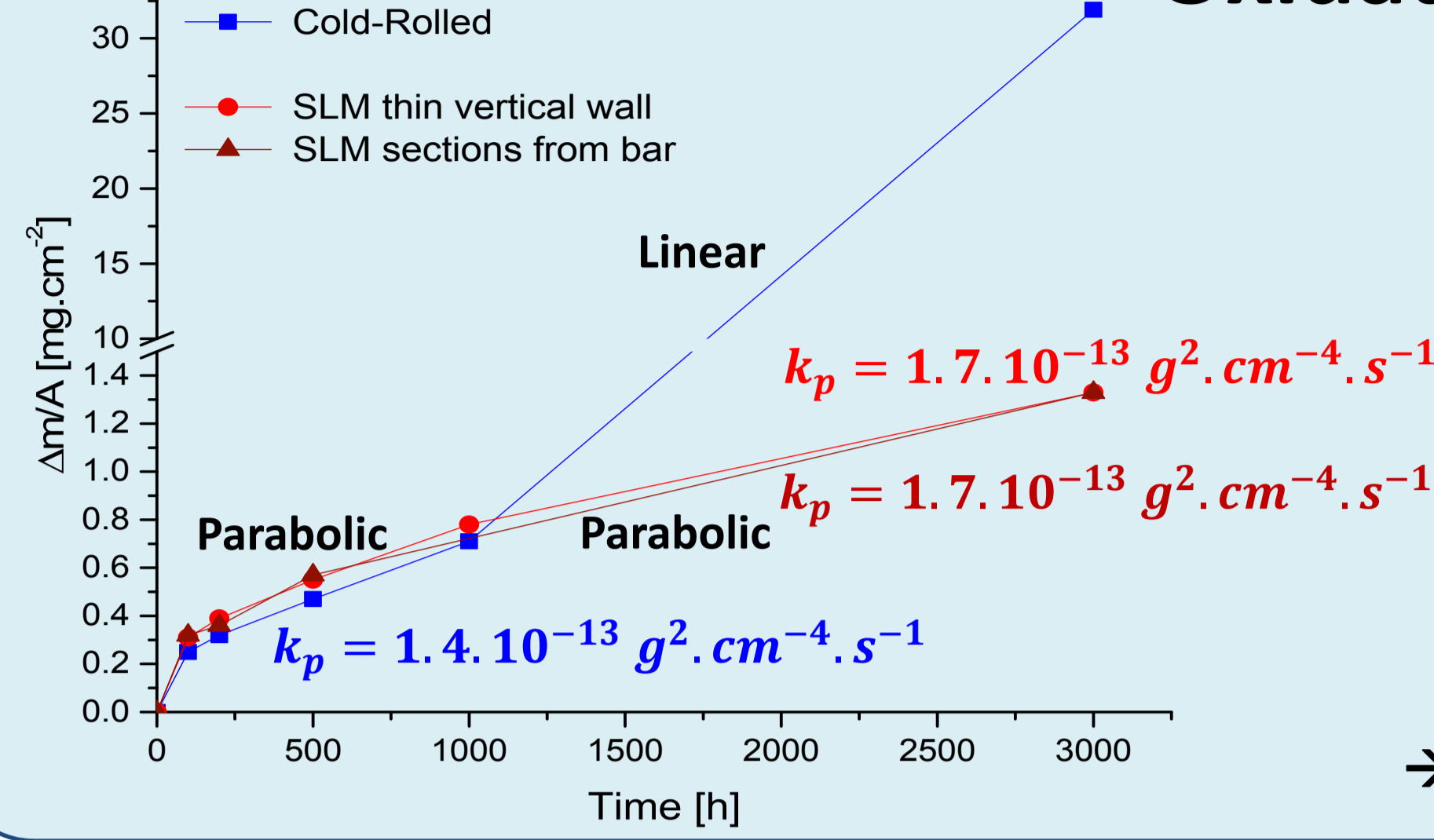
- Size: 10 * 10 * 1 mm
- SiC polishing up to 1000 grit
- Ultrasonic cleaning in ethanol



High temperature oxidation tests

- Muffle furnace
- Temperature: 900°C
- Atmosphere: Laboratory air
- Time: from 100 to 3000h

Oxidation kinetics



Protective oxides: parabolic kinetics $\left(\frac{\Delta m}{A}\right)^2 = k_p t$
 $k_p \equiv$ parabolic constant rate

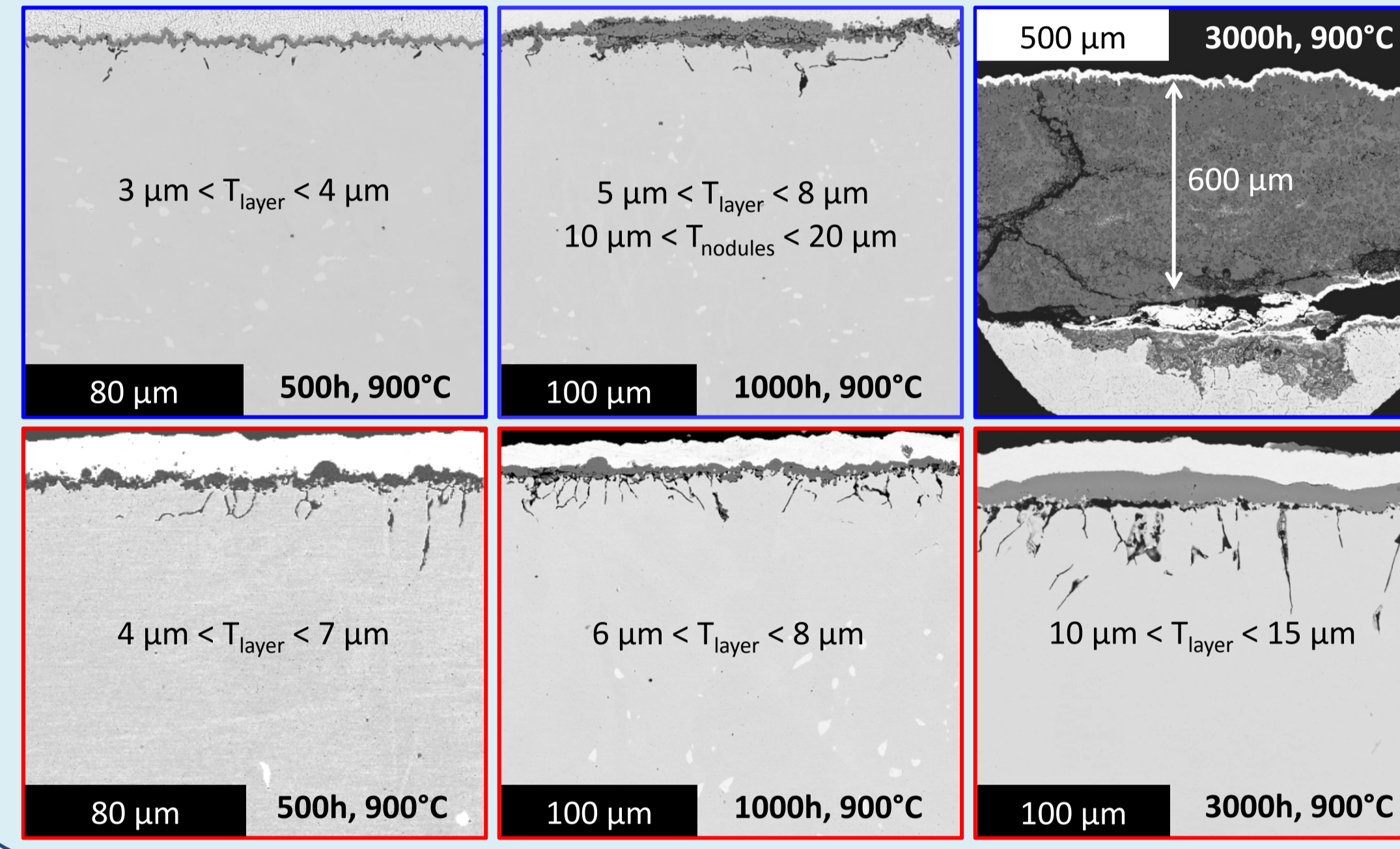
Non protective oxides: linear kinetics $\frac{\Delta m}{A} = k_l t$
 $k_l \equiv$ linear constant rate

- ✓ $k_p(\text{SLM}) \approx k_p(\text{cold-rolled})$ up to 1000h
- ✓ Breakaway oxidation only for cold-rolled samples after 1000h
- ✓ Parabolic behaviour throughout 3000 hours for SLM samples

→ Better behaviour for SLM samples during 3000h of exposure in air at 900°C

Oxides scales characterization

SEM cross-section observations



✓ Oxides thickness \nearrow when exposure time \nearrow

Rolled samples:

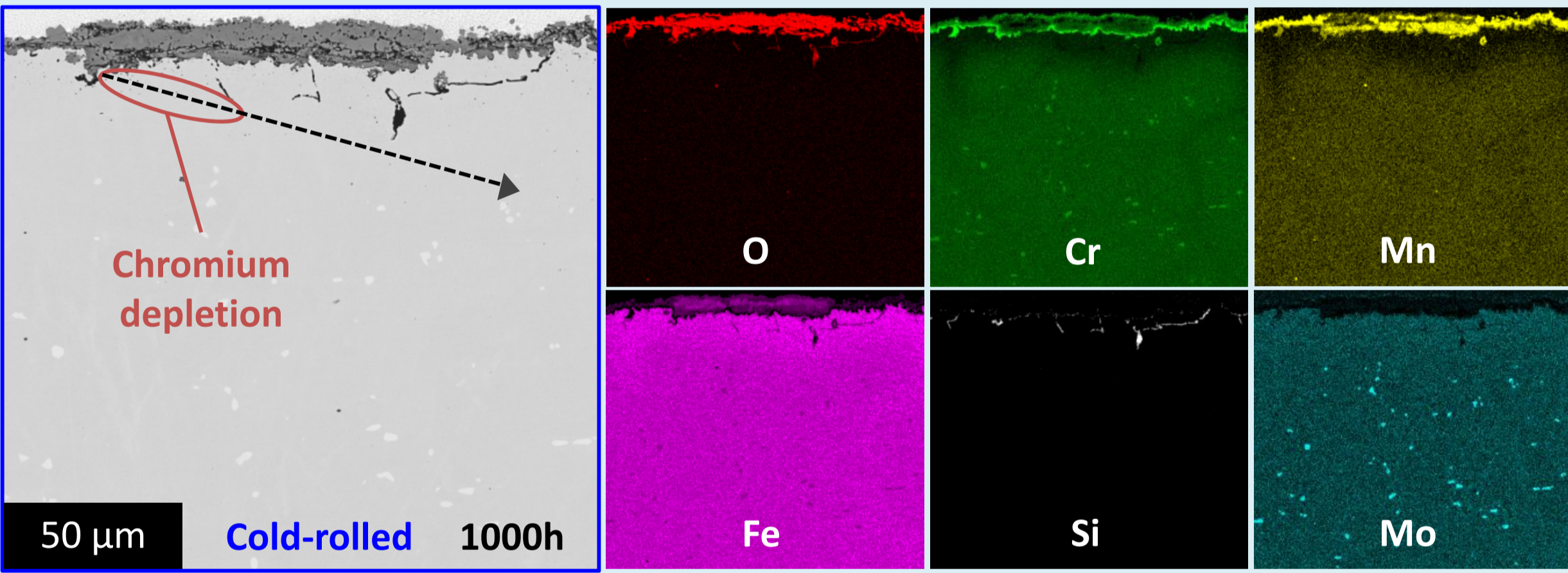
- ✓ Presence of non-protective iron nodule oxides ($\text{Fe, Cr}_2\text{O}_3 / \text{Fe}_3\text{O}_4$) after 1000h of exposure
- ✓ Very thick iron oxide layer and disastrous internal oxidation after 3000h

SLM samples:

- ✓ thin oxide layers: $\approx 12 \mu\text{m}$ after 3000h of exposure
- ✓ Protective scale composed of Cr_2O_3 for SLM coupons

Metal substrate evolution during high temperature exposure (SEM)

Rolled samples: 1000h of exposure at 900°C



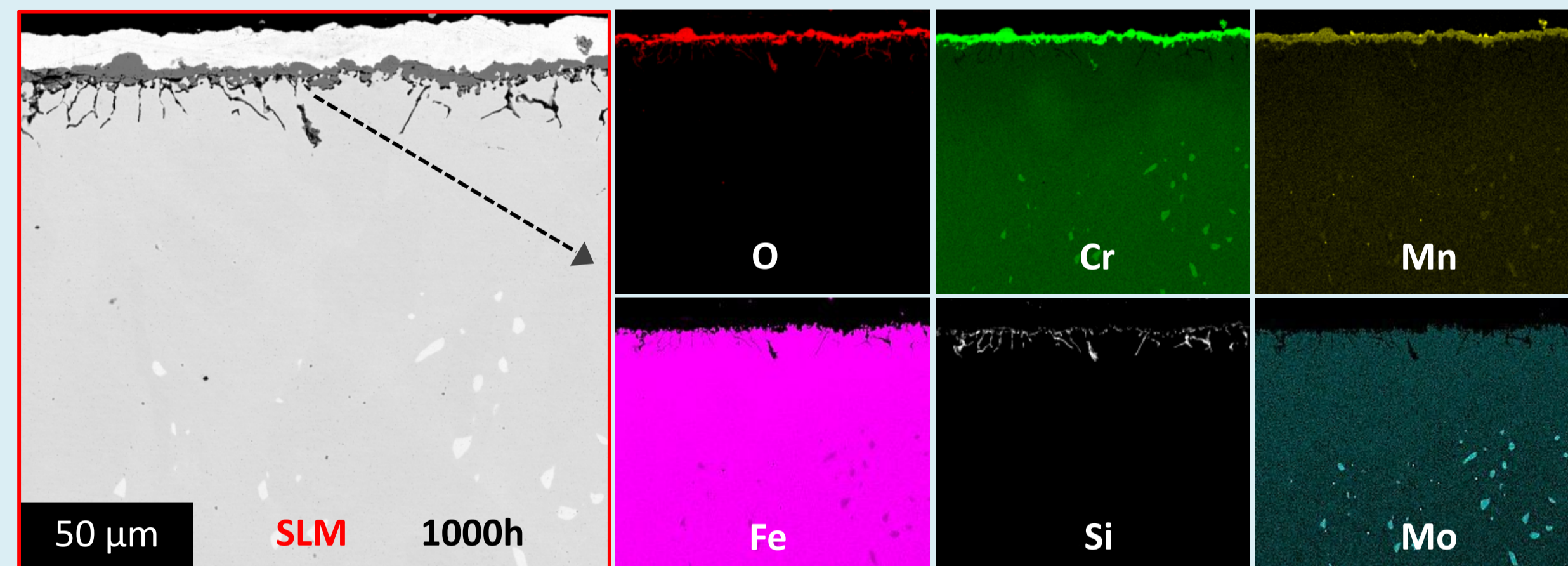
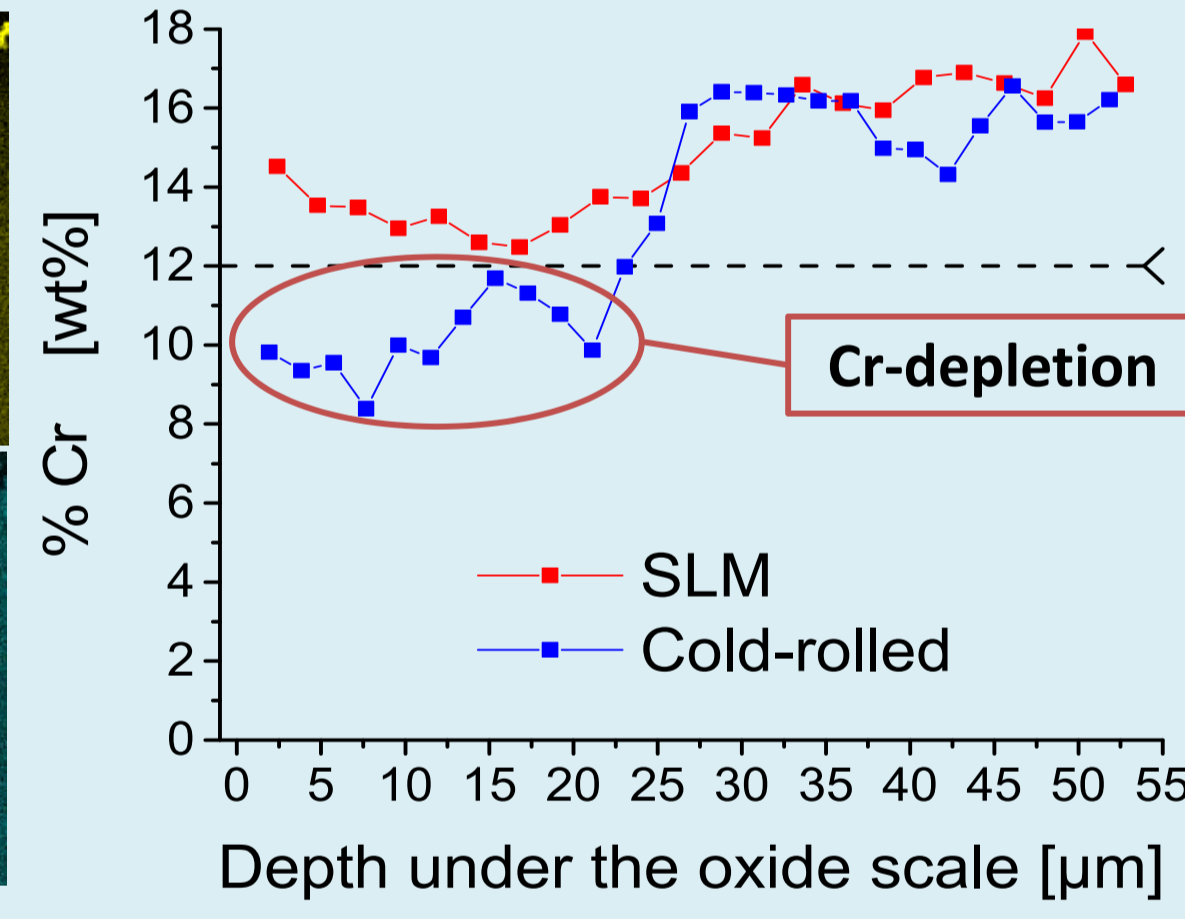
✓ Cr-depletion below 12%wt at the outer part of the metal (in the first 20 µm): protective scale cannot form anymore

→ Very good resistance against long term high temperature oxidation for SLM can be related to a sufficient supply of chromium from bulk to the surface which allows the formation of a protective chromia layer Cr_2O_3 .

Cr present at the outer part of the metallic substrate is consumed by the growth of Cr_2O_3 during the high temperature oxidation. Its recovery depends on the diffusion from bulk. This diffusion is known to depend on the mechanical conditioning of the surface and on the presence of defects such as precipitates and dislocations [3].

*12%mass is the lower limit of which chromia formation is favoured [4]

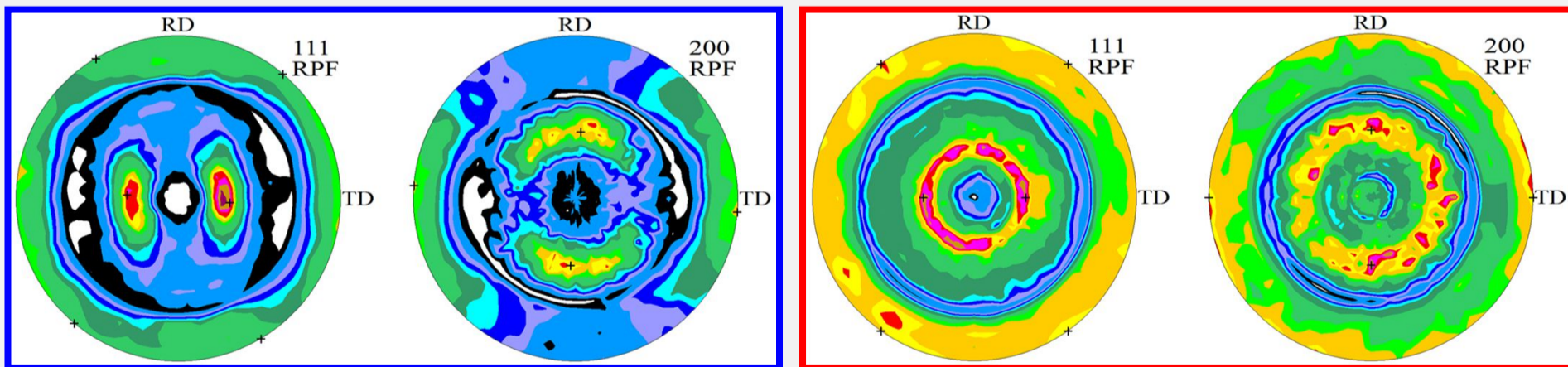
SLM samples: 1000h of exposure at 900°C



✓ Cr-content does not decrease below the 12%wt for SLM coupons

Characterisation of raw samples

Crystallographic Texture (XRD)



"Brass" texture {110} <-12>, planes {110} oriented // to the rolling surface

Fiber texture, planes {110} oriented // to the building platform.

→ Similar crystallographic textures: crystallographic planes {110} // to the surface exposition → Texture does not explain the reactivity difference

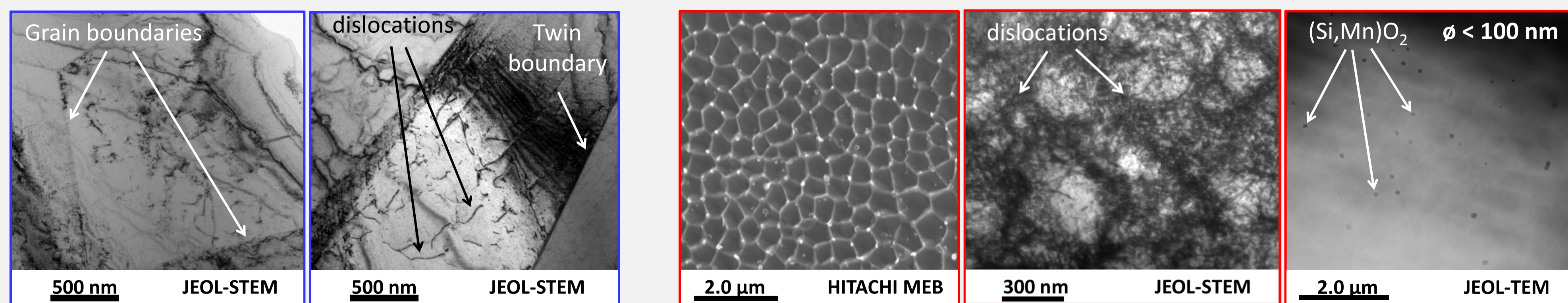
Mechanical surface state: Residual stresses (XRD)

Sample	Cold-rolled		SLM wall		SLM from pillar	
	σ_{11}	σ_{22}	σ_{11}	σ_{22}	σ_{11}	σ_{22}
Stresses [MPa]	-494 ± 57	-135 ± 22	-90 ± 27	-93 ± 44	-275 ± 30	-227 ± 19

σ_{11} = Rolling direction

→ The mechanical surface condition of the samples does not explain the differences in behavior between cold-rolling and SLM

Nano-scale characterization (TEM)



✓ Microstructure with polyhedral grains accompanied by twins and some isolated dislocations

✓ Cellular grain sub-structure formed by the accumulation of a large number of dislocation accompanied by nano-inclusions

→ Higher amount of dislocations for SLM than rolled samples
→ Larger number of dispersed nanoparticles only in the case of SLM samples

Dislocations act as a diffusion short-circuit for Cr in the substrate [3,5] and thus facilitate the diffusion of chromium from bulk to the surface of the samples.

Nano-inclusions may equally improve corrosion resistance [6].

Conclusions

- Promising results after oxidation under air of laboratory for SLM samples
- Differences in term of reactivity and corrosion products
 - ❖ Parabolic behavior for SLM throughout 3000 hours
 - ❖ Parabolic behavior for cold-rolled only up to 1000 hours
 - Breakaway oxidation from 1000h for conventional coupons
 - Chromium depletion (< 12%wt) jut for as-rolled samples

The cellular network, formed by the accumulation of a large number of dislocations, as well as the presence of ultra-fine nanoparticles would improve the high-temperature behavior of stainless steel and explain the best behavior of SLM specimens.

Perspectives

- Quantify the dislocation content by XRD (modified Warren-Averbach method)
- Determined Cr diffusion coefficient from EDS-SEM profiles at the metal surface
- Confirm the better behaviour of SLM samples for longer exposure times and different temperature / atmospheres

References

- [1] F. Bartolomeu and al., *Additive Manufacturing*, vol. 16, p. 81-89, août 2017
- [2] D. Wang and al., *Materials & Design*, vol. 100, p. 291-299, juin 2016
- [3] J. Yuan and al., *Oxidation of Metals*, vol. 79, p. 541-551, 2013
- [4] S. Chevalier, *Traitements de surface et nouveaux matériaux*, Editions de l'Université de Dijon, 2007
- [5] H. J. Grabke and al., *Oxidation of Metals*, vol. 50, n° 3-4, p. 241-254, oct. 1998
- [6] J. Stubbins and al., <https://doi.org/10.2172/1179825>, 2015