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C. Duhamel, M. Sennour, Frédéric Georgi, C. Guerre, E. Chaumon, et al.. Characterization of oxide scales formed on Alloy 82 in nominal PWR primary water at 340 degrees C and in hydrogenated steam at 400 degrees C. USNRC 2015 Meeting – International Cooperative Group for Environmentally Assisted Cracking, May 2015, Ann Harbor, United States. cea-02500813

HAL Id: cea-02500813

<https://cea.hal.science/cea-02500813v1>

Submitted on 12 Jun 2020

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Characterization of oxide scales formed on Alloy 82 in nominal PWR primary water at 340°C and in hydrogenated steam at 400°C

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SCC of Alloy 82

Initiation tests performed in hydrogenated steam at 400°C

- SCC initiation is difficult in Alloy 82 → test acceleration
- Previous results on Alloy 600 show that :
 - Stress corrosion cracks exhibit similar features
 - Trend between heats is respected
 - Same activation energy for initiation

} Hydrogenated steam 400°C
VS
Primary water 360°C

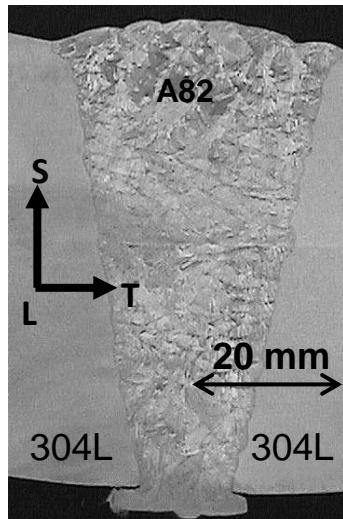
1. Representativeness of SCC tests in hydrogenated steam

2. Description of the oxide scale formed on Alloy 82

- Effect of weld (composition and/or welding process)
- Effect of thermal treatment

Materials and oxidation conditions

	C	Si	Mn	P	S	Cu	Mo	Ni	Cr	Co	Nb	Ti	Fe
RCC-M	<0.1	<0.5	2.5/3.5	<0.03	<0.015	<0.5	-	>67	18/22	<0.1	2/3	<0.75	<3
Weld A	0.025	0.07	2.57	0.004	<0.001	<0.01	-	71.7	19.12	0.04	2.41	0.1	3.07
Weld B	0.014	0.17	2.88	0.002	0.017	<0.01	0.05	72.9	18.15	0.01	2.83	<0.01	2.3



Weld	A		B
Welding process	Gas tungsten arc welding (GTAW)		Flux core arc welding (FCAW)
Metallurgical state	As-welded	Thermally-treated 7h - 600°C	As-welded

Oxidation tests performed on coupons with 1 μm mirror finish in stainless steel autoclaves.

HYDROGENATED STEAM

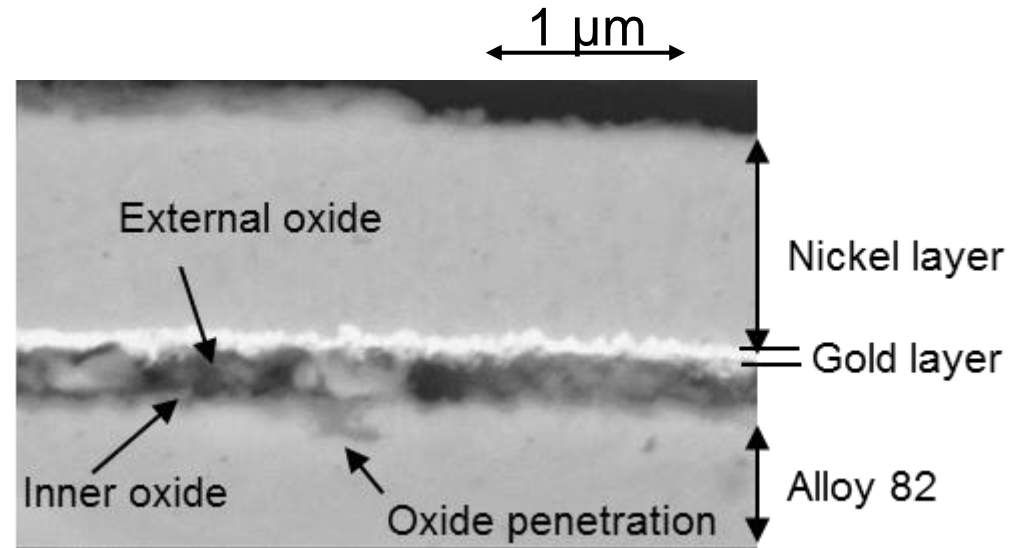
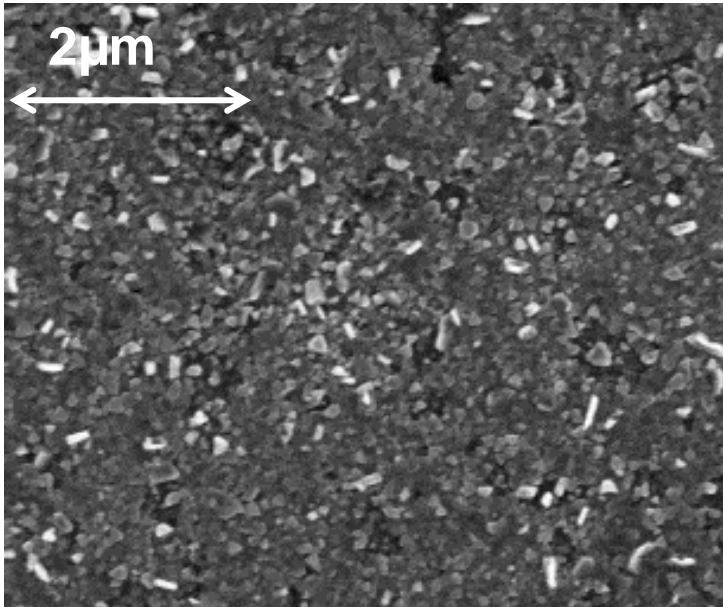
- 400°C
- $P_{\text{tot}} = 200 \text{ bar}$, $P(\text{H}_2) = 800 \text{ mbar}$
- 1500h / 2500h

PRIMARY WATER

- 340°C
- $[\text{H}_2] = 37 \text{ mL / kg H}_2\text{O}$
- 1500h / 2500h

Oxidation in hydrogenated steam at 400°C

Weld	A		B
Welding process	Gas tungsten arc welding (GTAW)		Flux core arc welding (FCAW)
Metallurgical state	As-welded	Thermally-treated 7h - 600°C	As-welded
Oxidation duration (h)	2500	1500/2500	2500



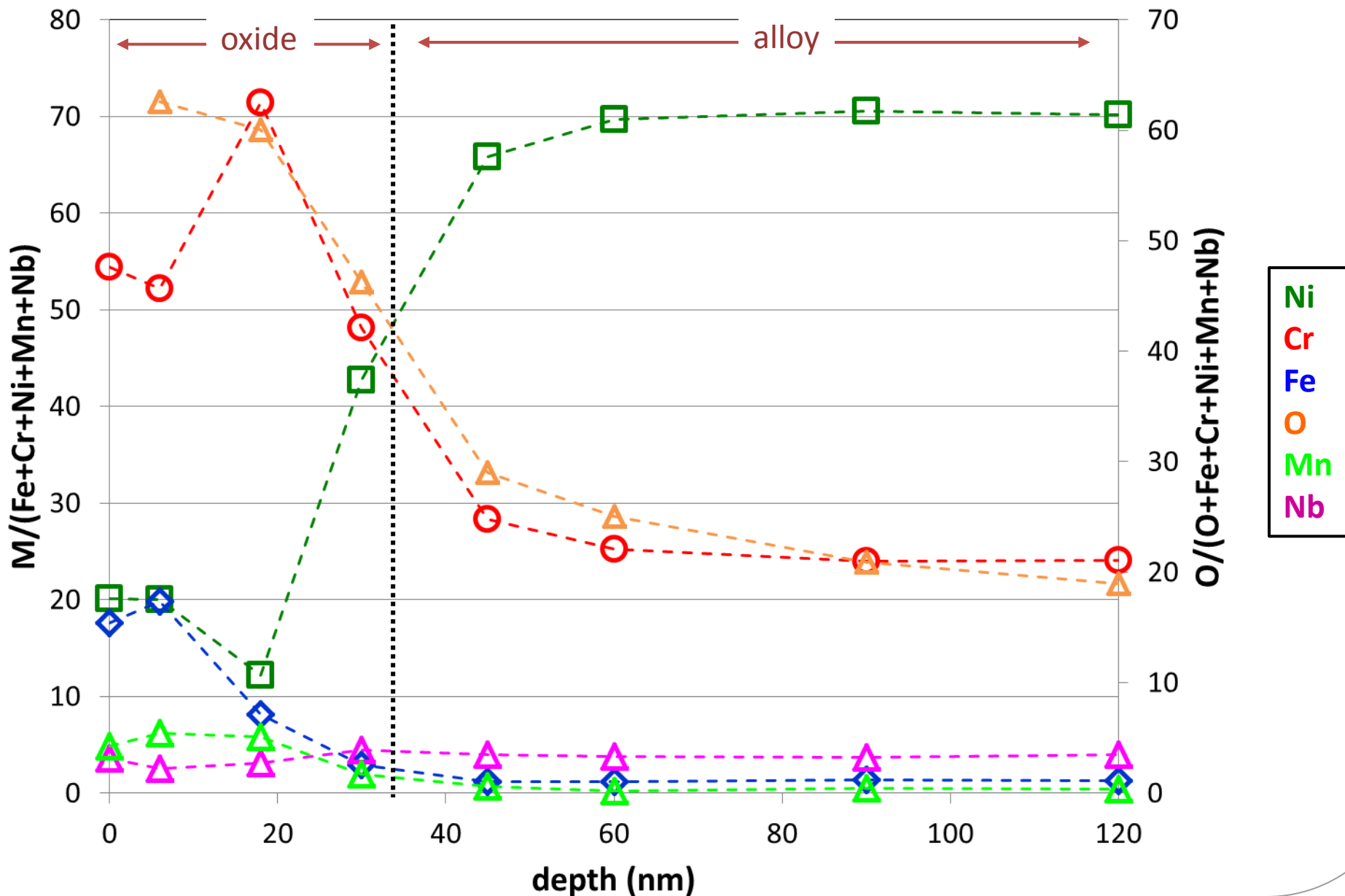
Duplex structure:

- Discontinuous outer layer with pyramidal and platelet-like crystallites
- Continuous inner layer

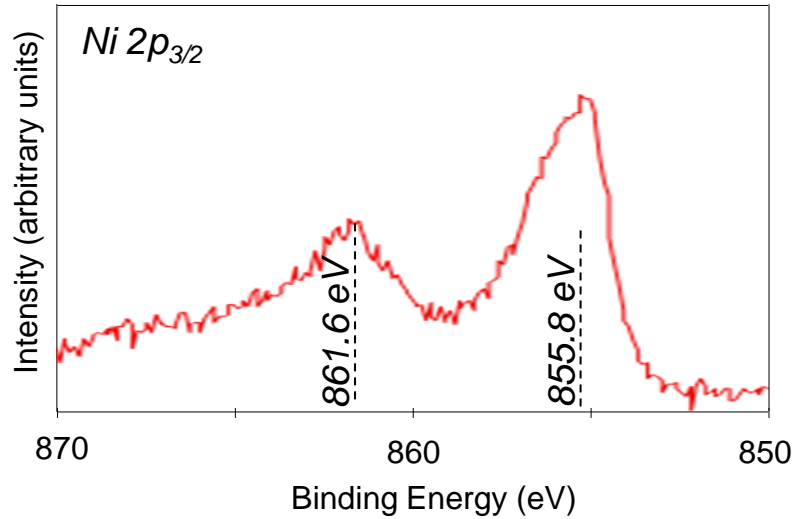
Oxide penetrations (depth < 500 nm)

XPS depth profiles

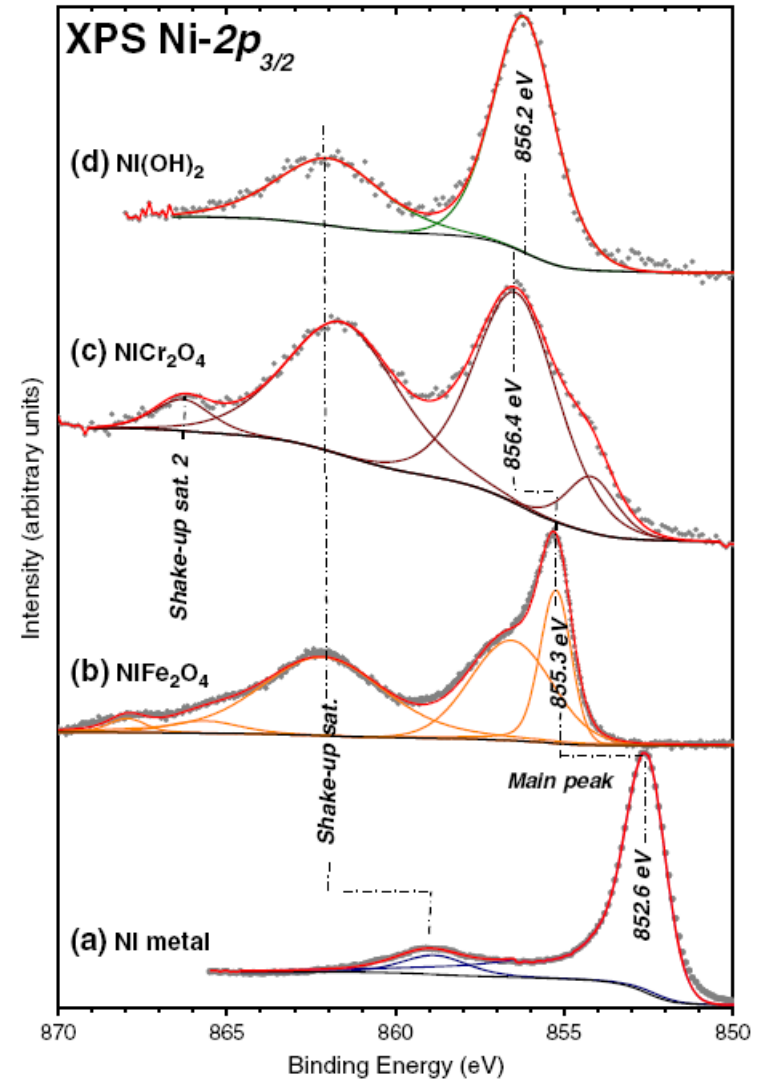
Hydrogenated steam
Weld A – AW – 2500h



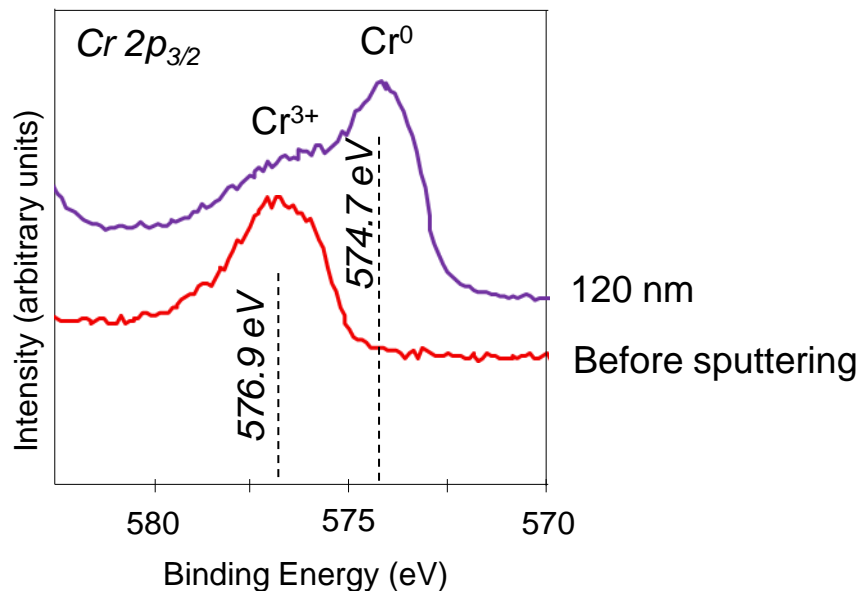
Before sputtering



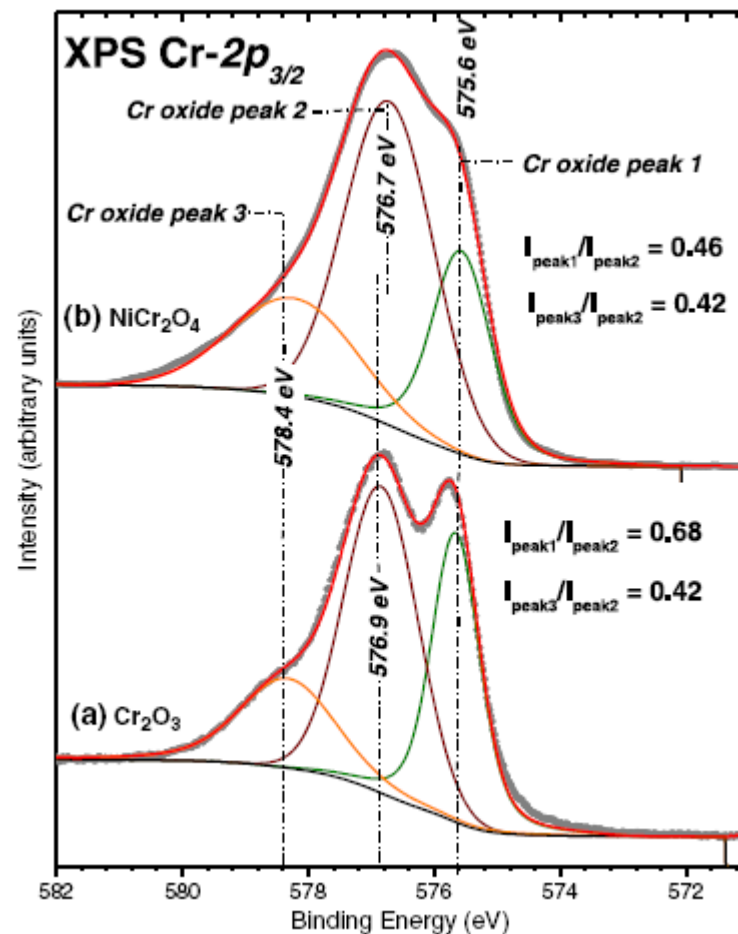
- Shape and binding energies consistent with NiFe₂O₄
- Ni(OH)₂ cannot be excluded



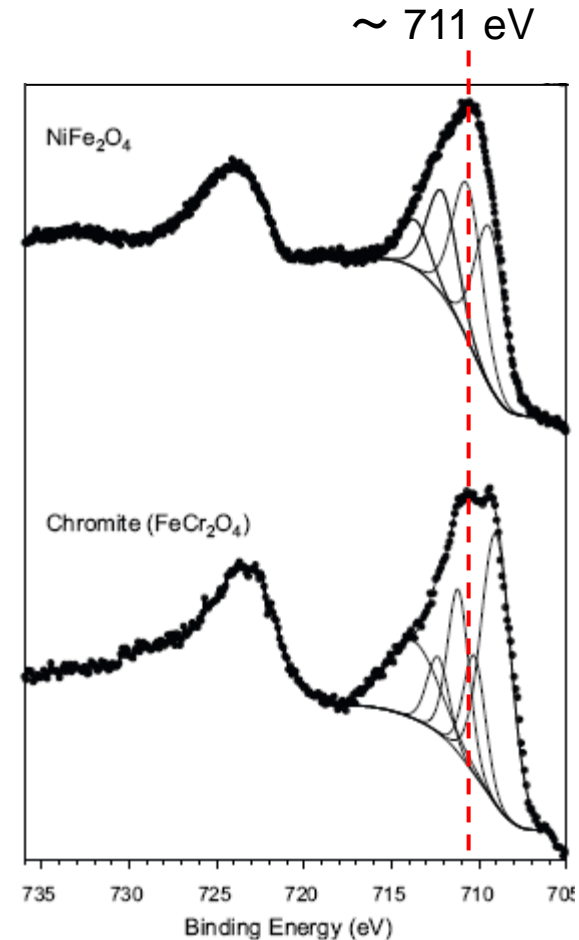
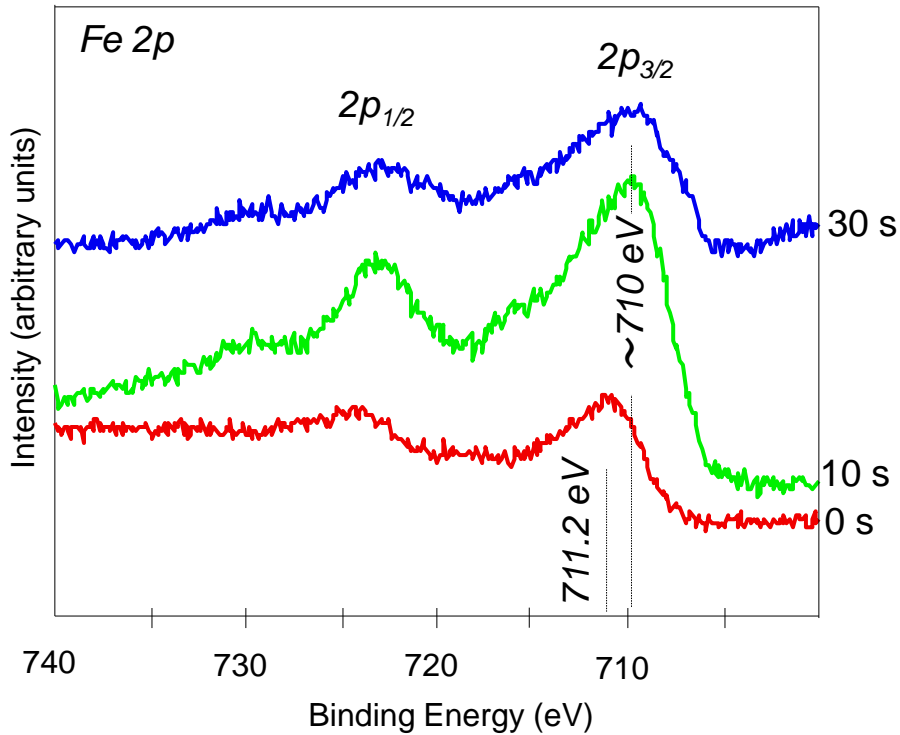
Marchetti et al. (2015)



- Before sputtering: hard to distinguish NiCr₂O₄ from Cr₂O₃
- Cr with the oxidation state +III is detected for the longest sputtering time



Marchetti et al. (2015)

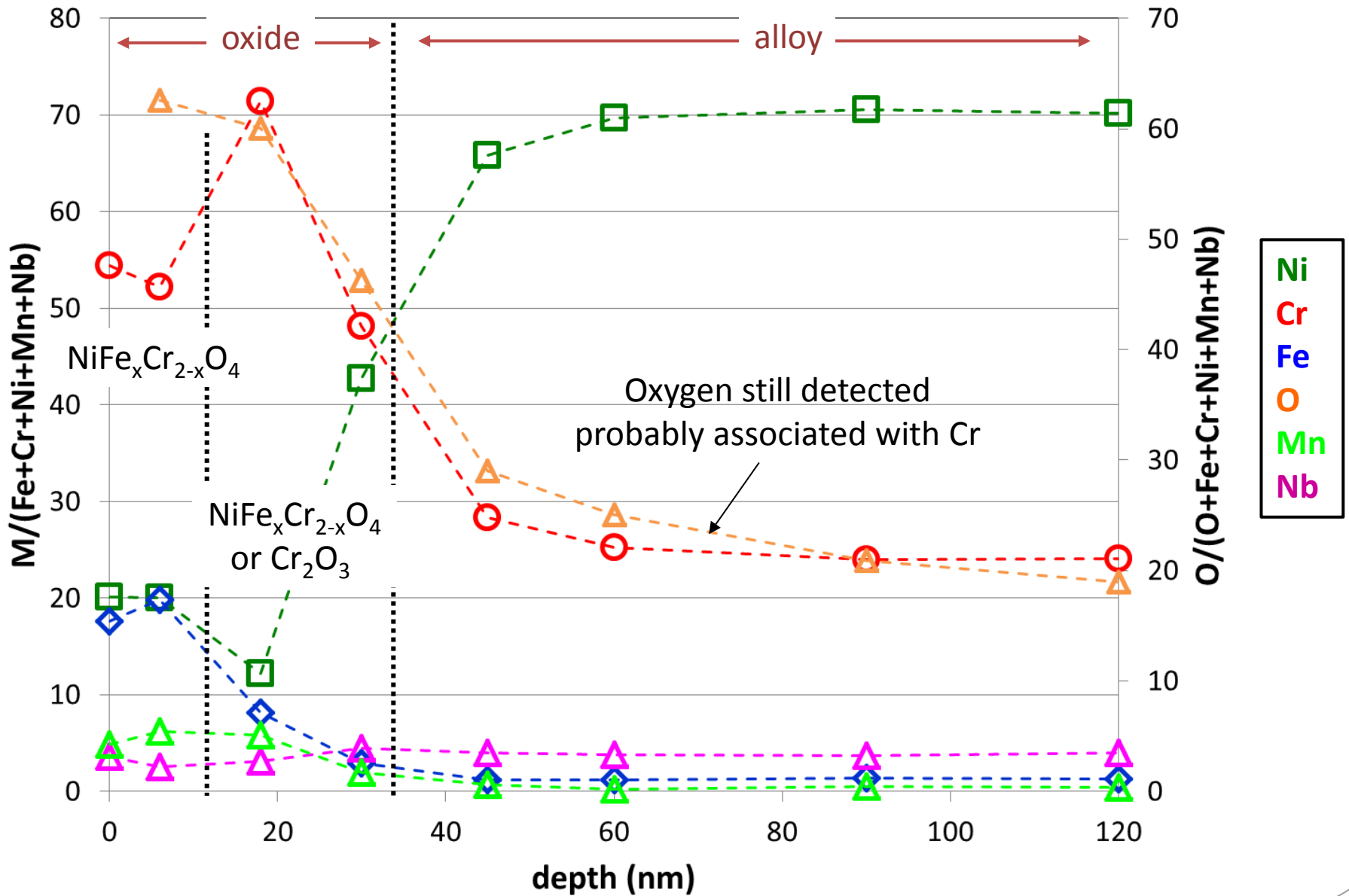


- Before sputtering:
consistent with NiFe_xCr_{2-x}O₄ or Fe_xCr_{3-x}O₄
- Slight shift towards lower energies:
 - Fe/Cr \searrow in NiFe_xCr_{2-x}O₄? *Allen et al (1989)*
 - Fe (III) \rightarrow Fe (II)? *McIntyre et al. (1977)*

Biesinger et al. (2011)

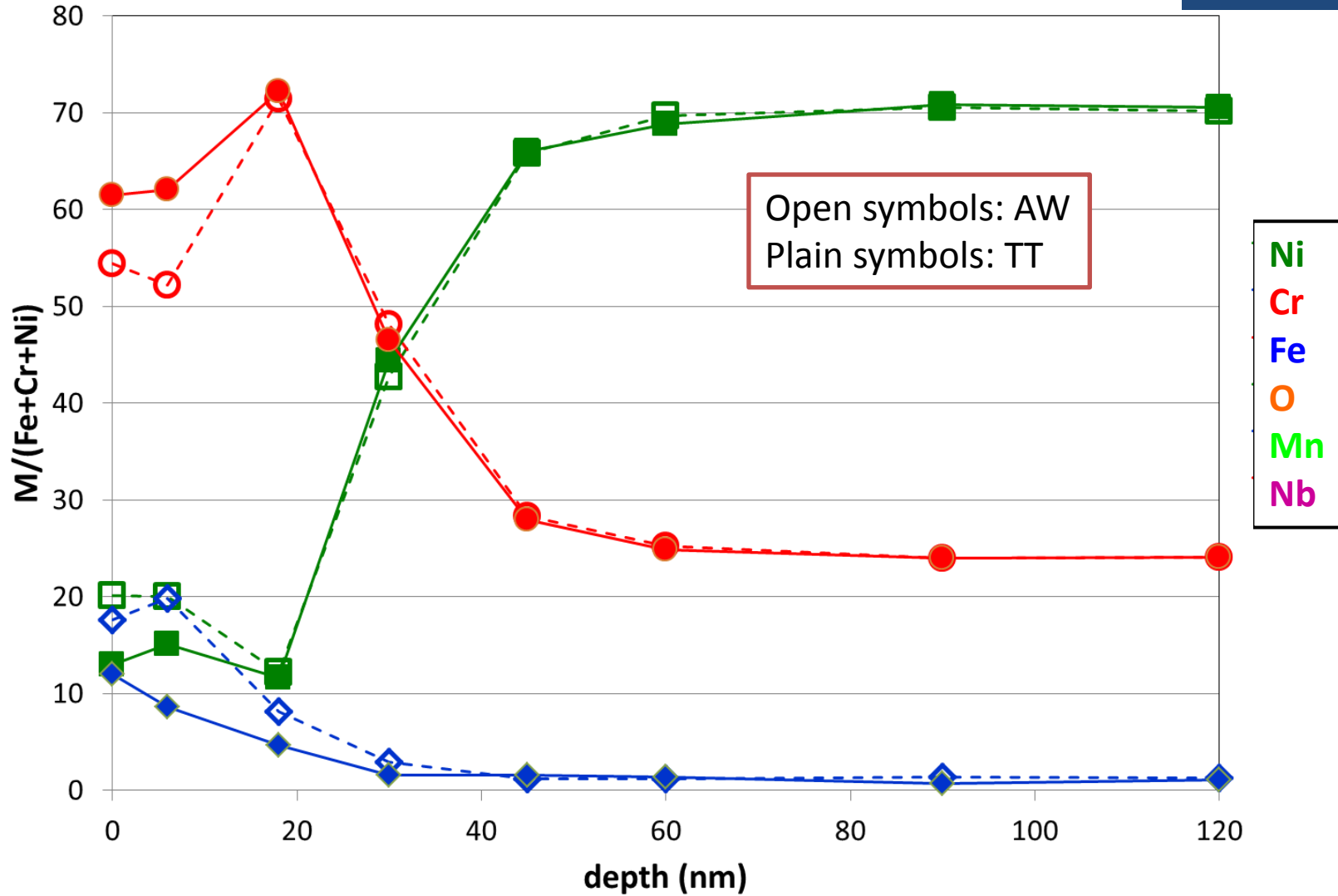
XPS depth profiles

Hydrogenated steam
Weld A – AW – 2500h



XPS depth profiles

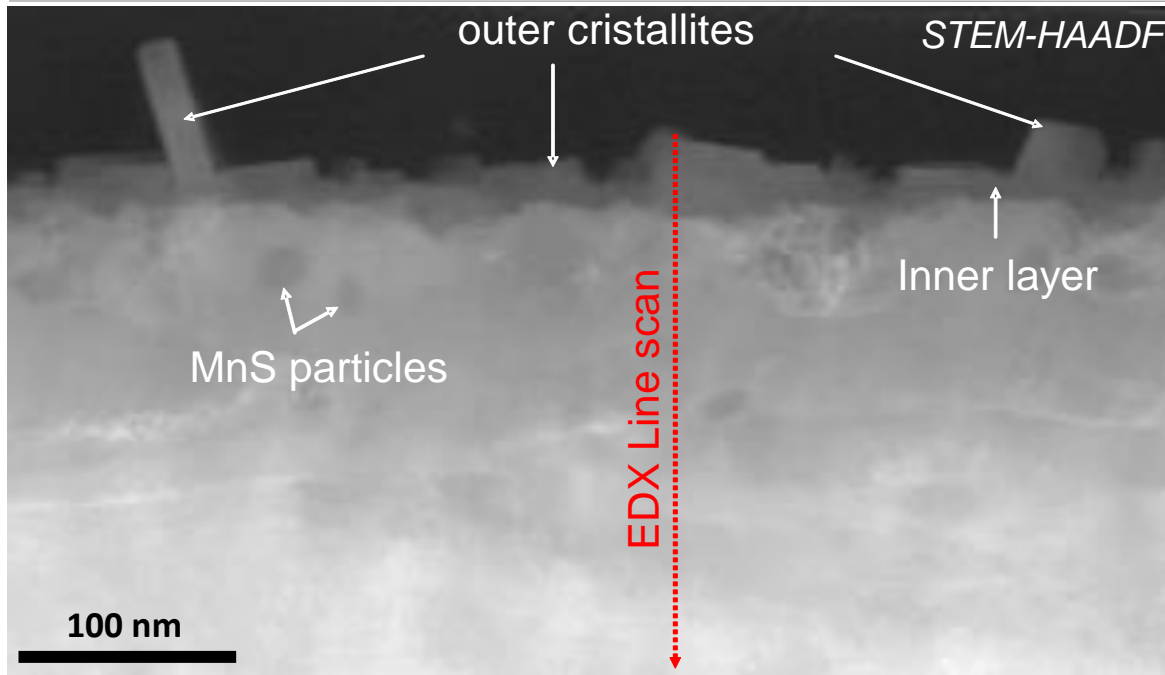
Hydrogenated steam
Weld A – AW – 2500h
Weld A – TT – 2500h



Similar results for all the samples

TEM analyses

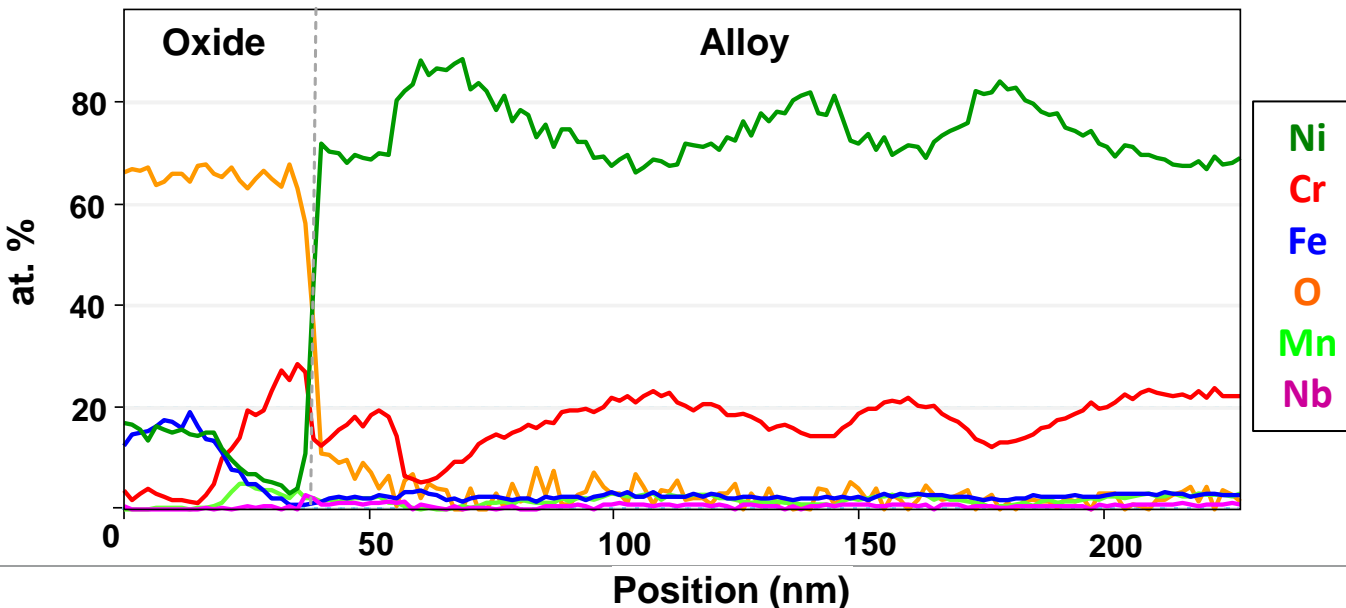
Hydrogenated steam
Weld A – AW – 2500h



Outer layer:
Ni- and Fe-rich crystallite

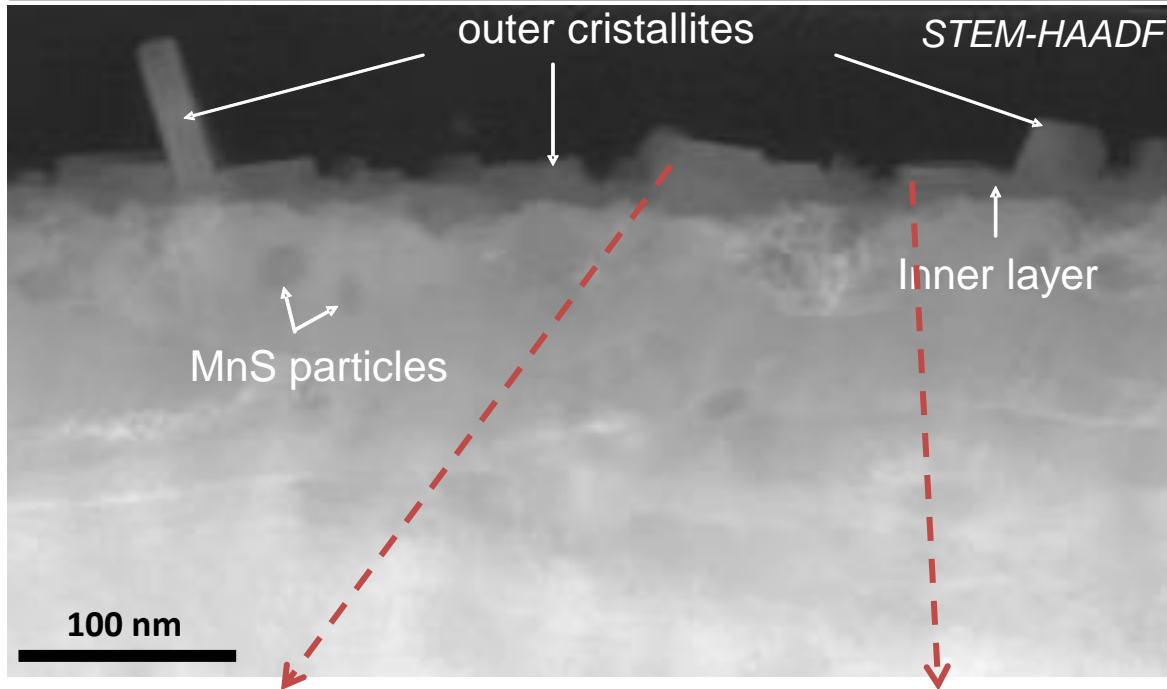
Inner layer:
Cr-rich
Small amounts of Mn

Alloy:
Fluctuation of composition
Strong localized Cr depletion

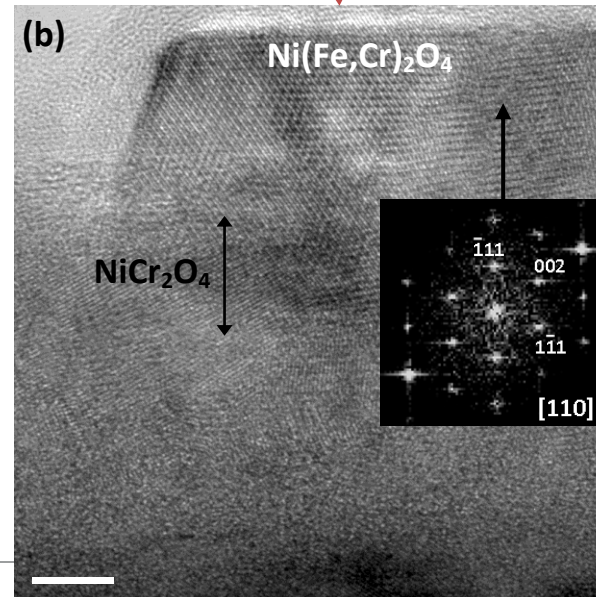
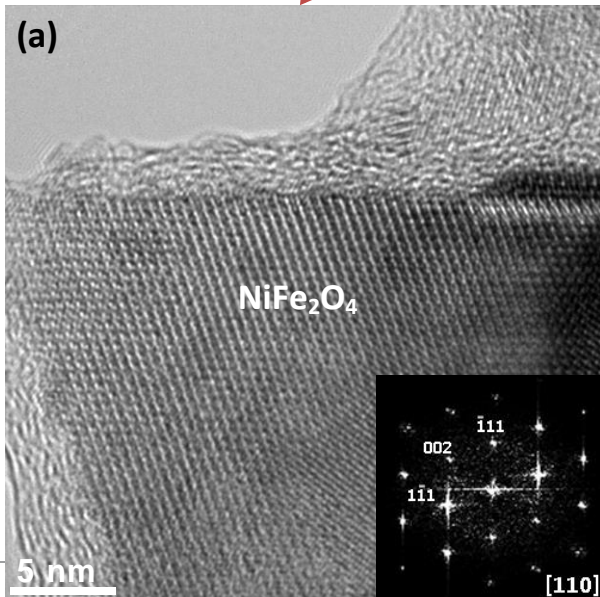


TEM analyses

Hydrogenated steam
Weld A – AW – 2500h

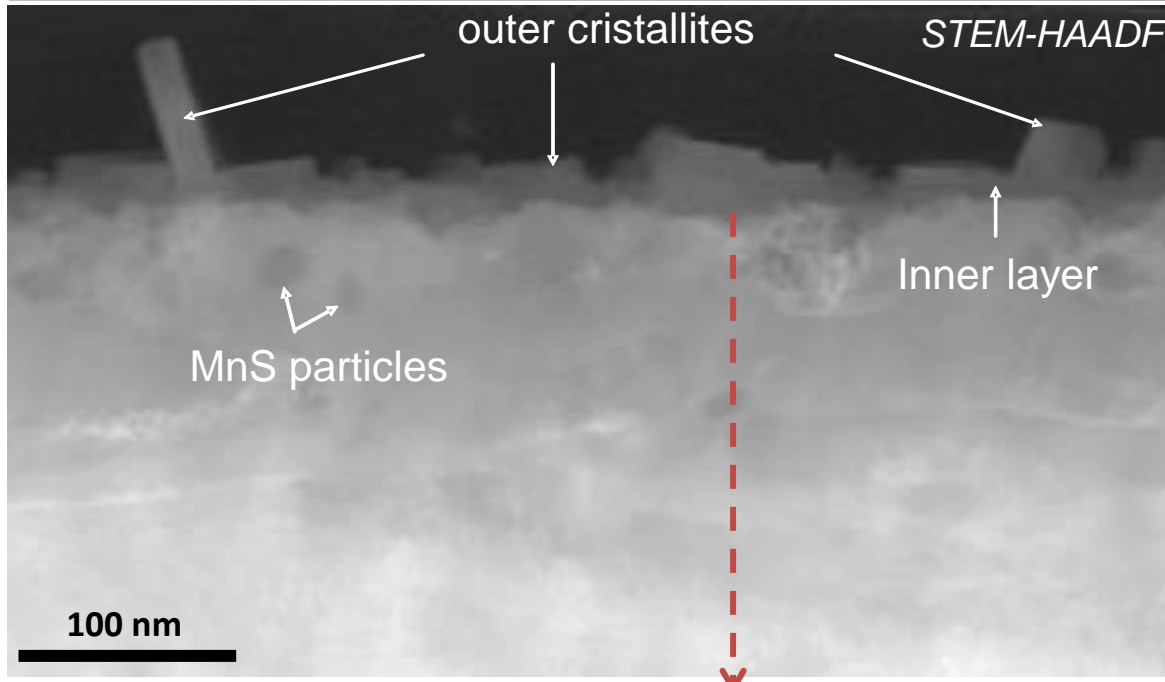


Outer layer:
 NiFe_2O_4 / $\text{NiFe}_x\text{Cr}_{2-x}\text{O}_4$



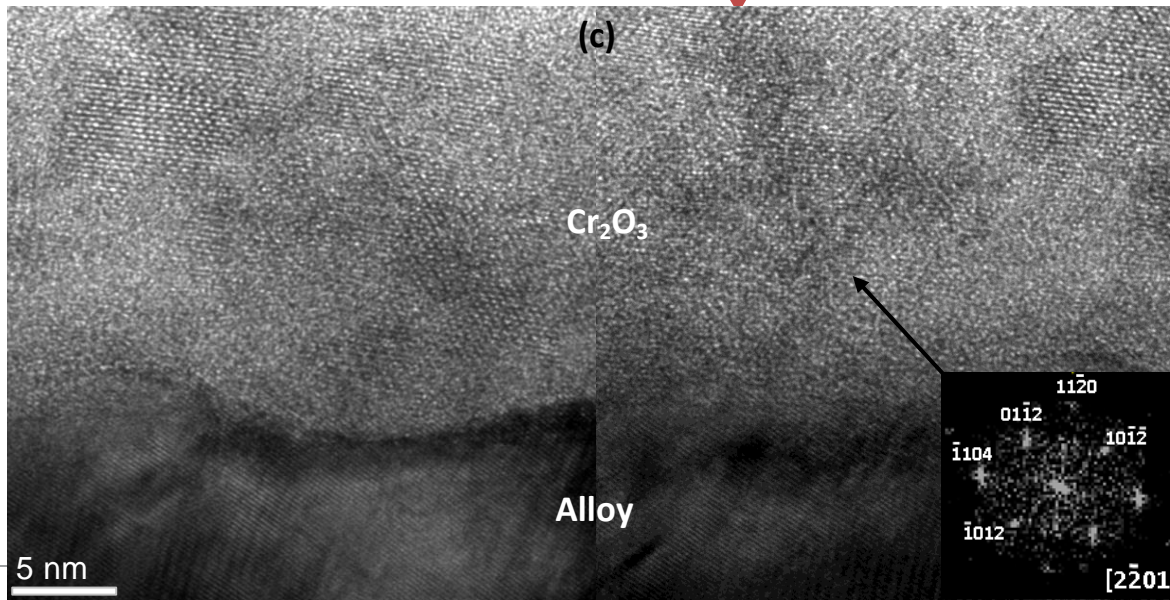
TEM analyses

Hydrogenated steam
Weld A – AW – 2500h



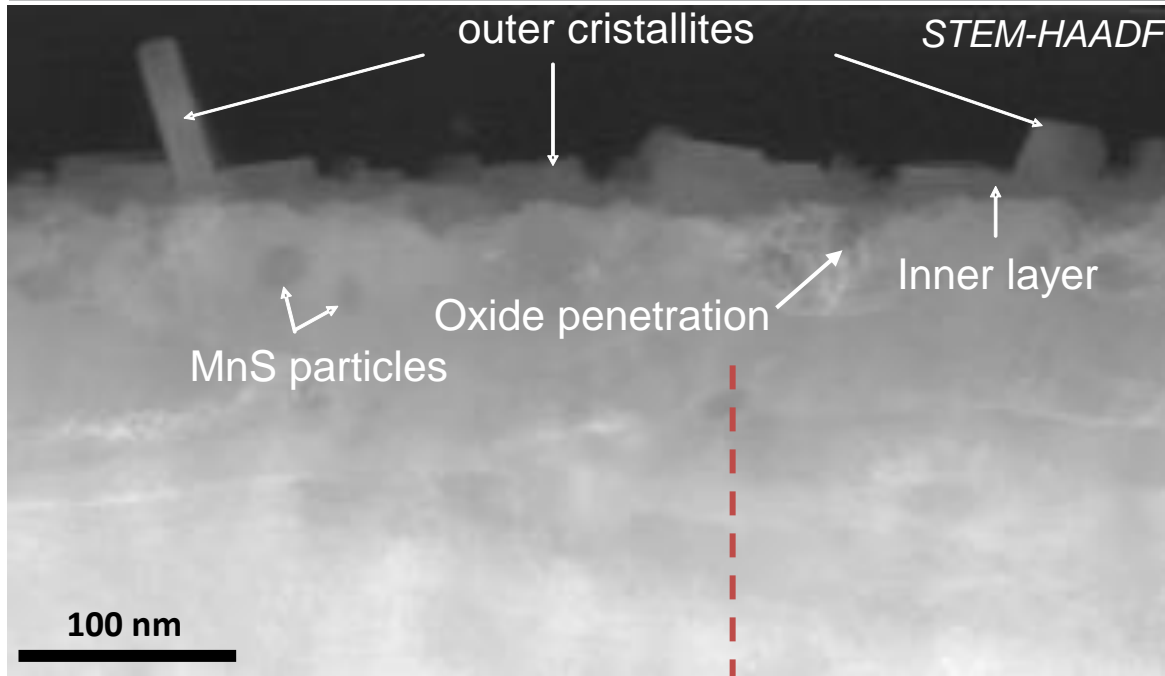
Outer layer:
 $\text{NiFe}_2\text{O}_4 / \text{NiFe}_x\text{Cr}_{2-x}\text{O}_4$

Inner layer:
- NiCr_2O_4
- Cr_2O_3



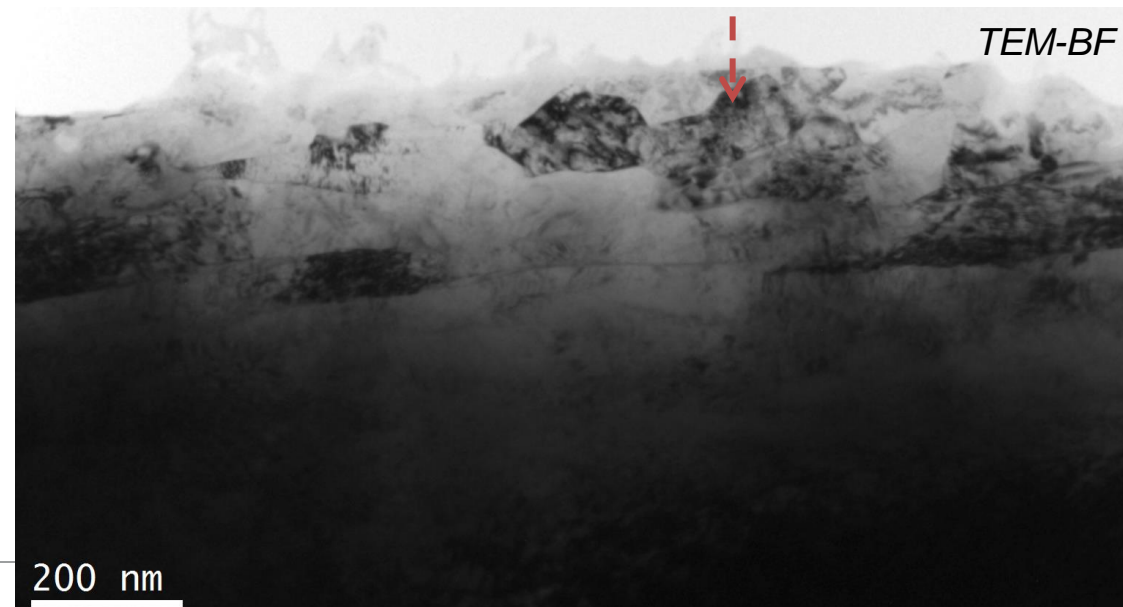
TEM analyses

Hydrogenated steam
Weld A – AW – 2500h



Outer layer:
 NiFe_2O_4 / $\text{NiFe}_x\text{Cr}_{2-x}\text{O}_4$

Inner layer:
- NiCr_2O_4
- Cr_2O_3



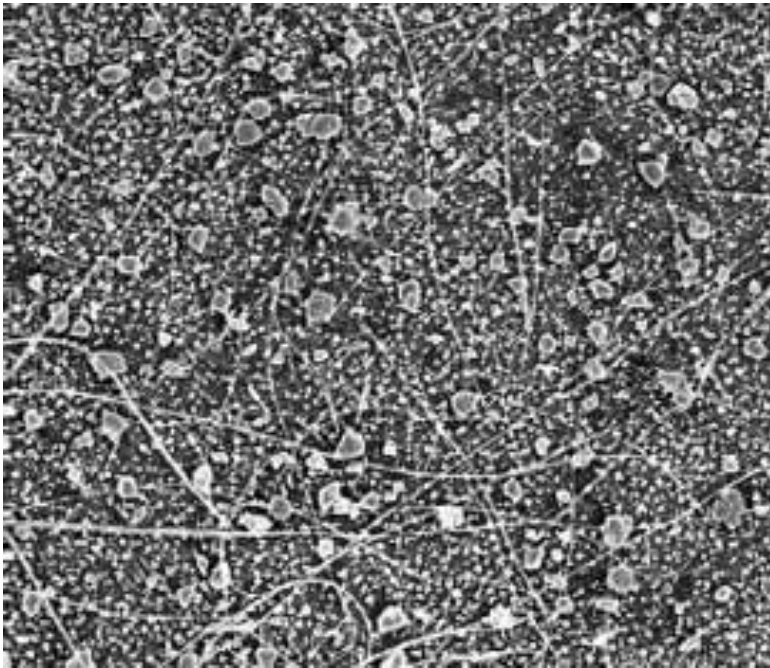
Alloy:
Recrystallized sub-layer
Thickness: 150 – 300 nm
Nanograins: varying composition

Oxidation in primary water at 340°C

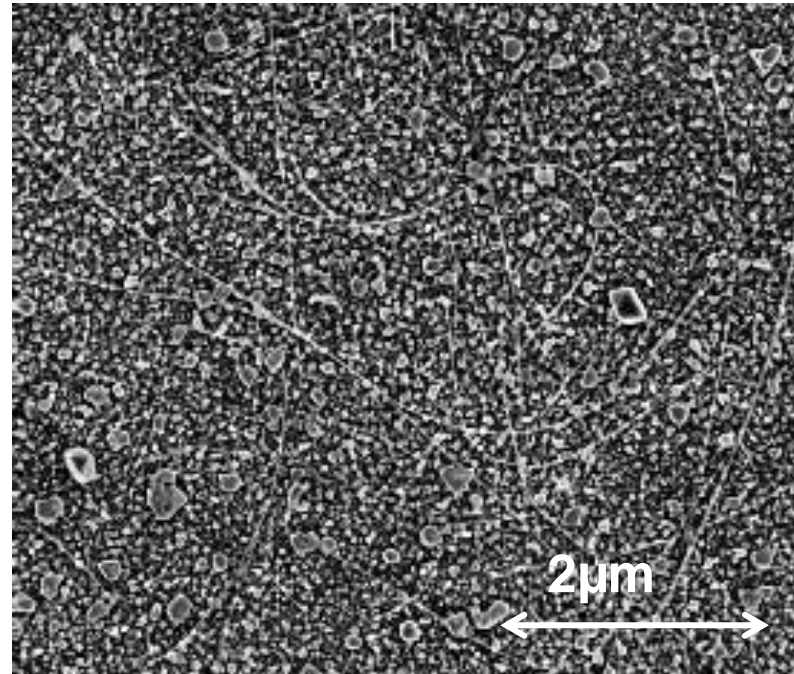
Weld	A	
Welding process	Gas tungsten arc welding (GTAW)	
Metallurgical state	As-welded	Thermally-treated 7h - 600°C
Oxidation duration (h)	1500	1500

SEM observations

As-welded



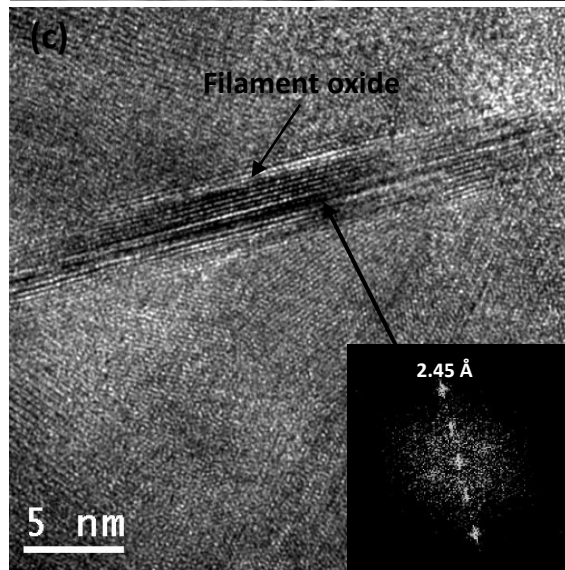
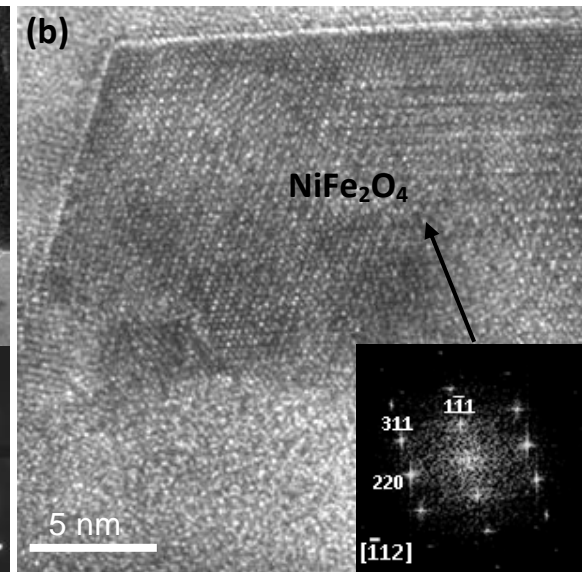
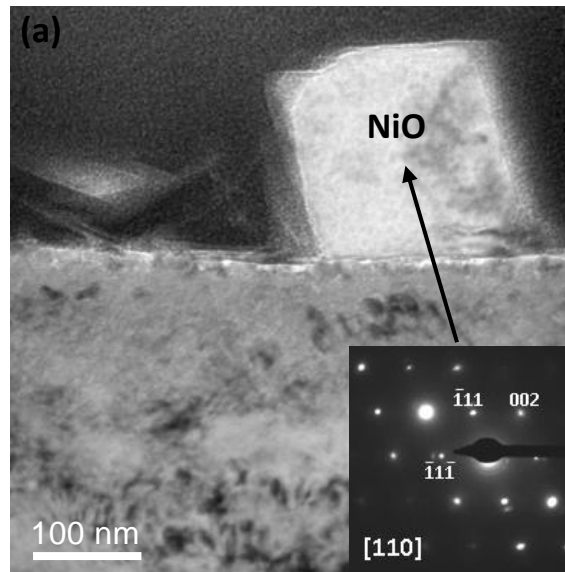
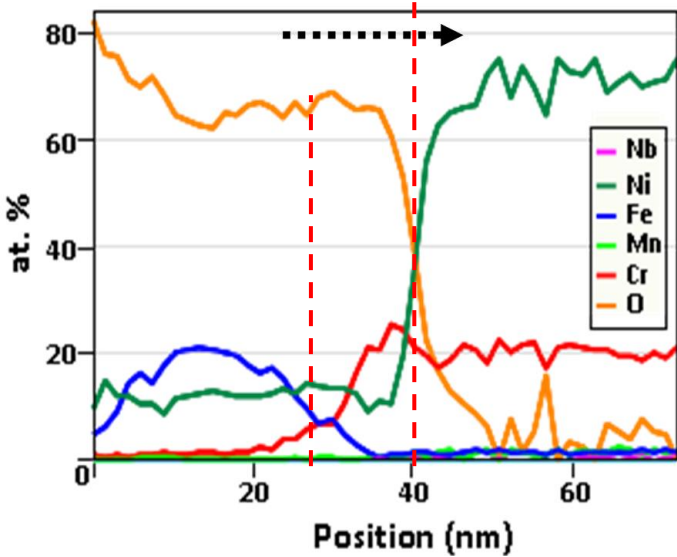
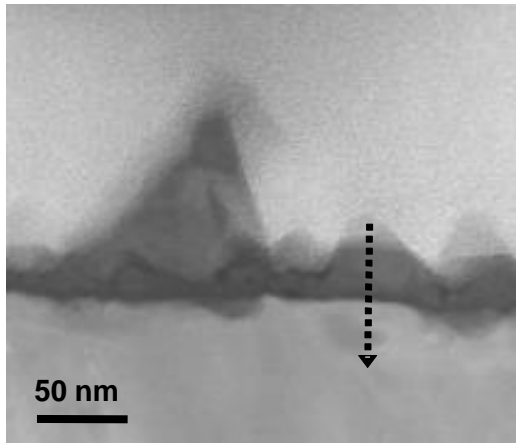
Heat-treated



Discontinuous outer layer with pyramidal crystallites and filaments

Heat-treated sample

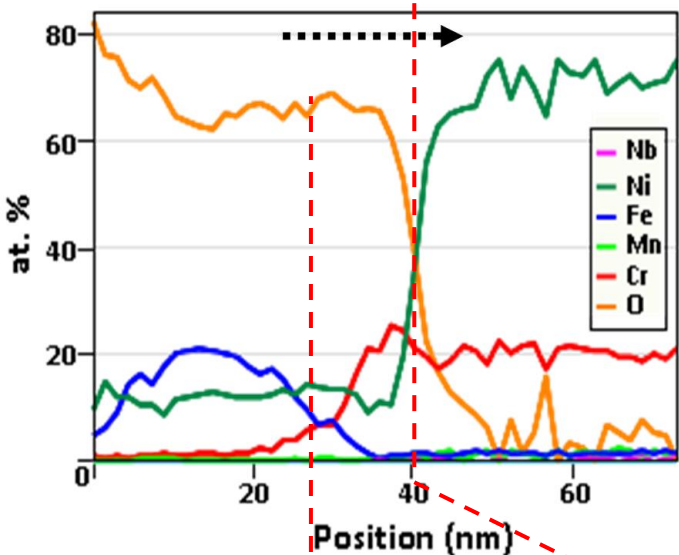
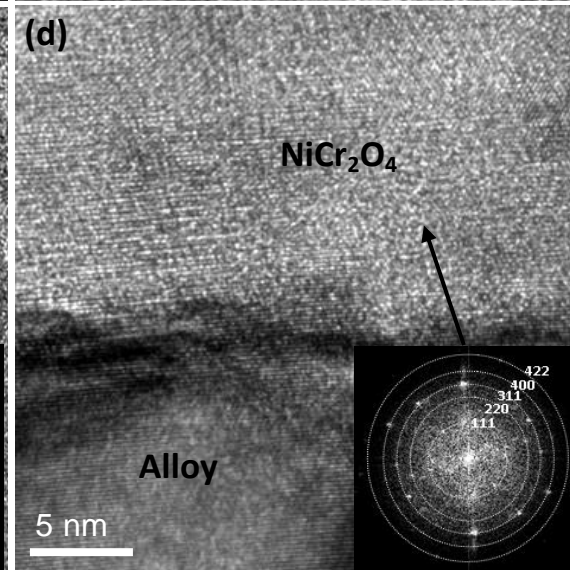
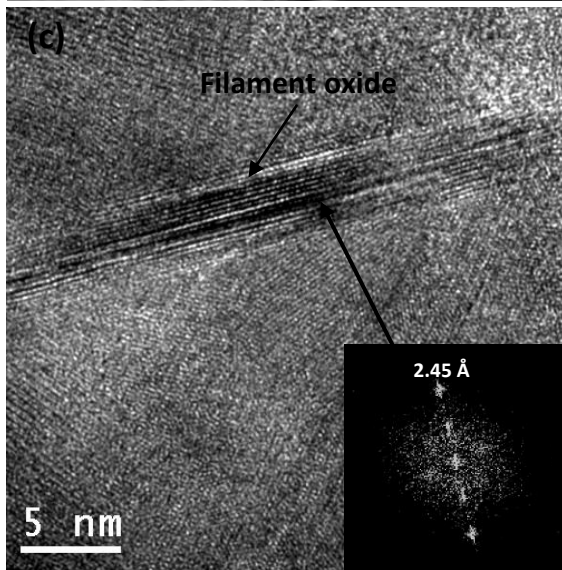
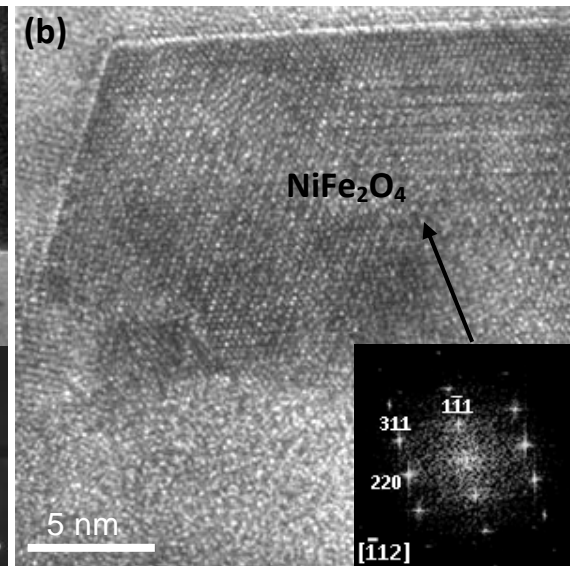
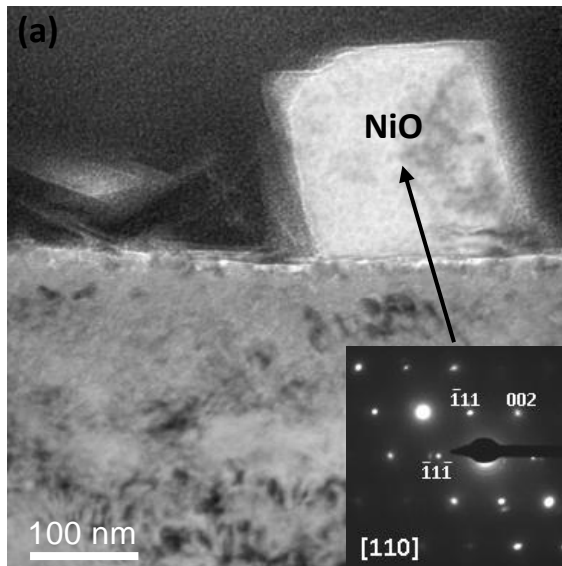
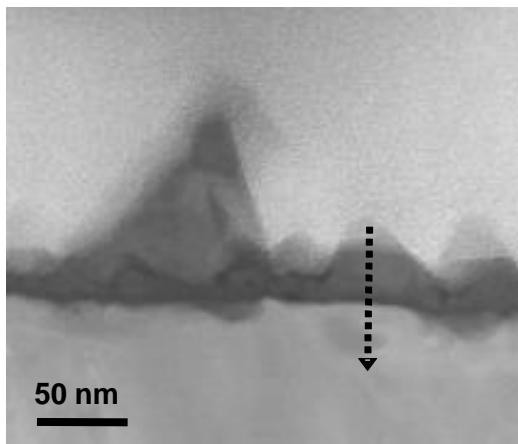
Primary water
Weld A – TT – 1500h



- Outer layer
- NiFe_2O_4
 - NiO
 - filament

Heat-treated sample

Primary water
Weld A – AW – 1500h

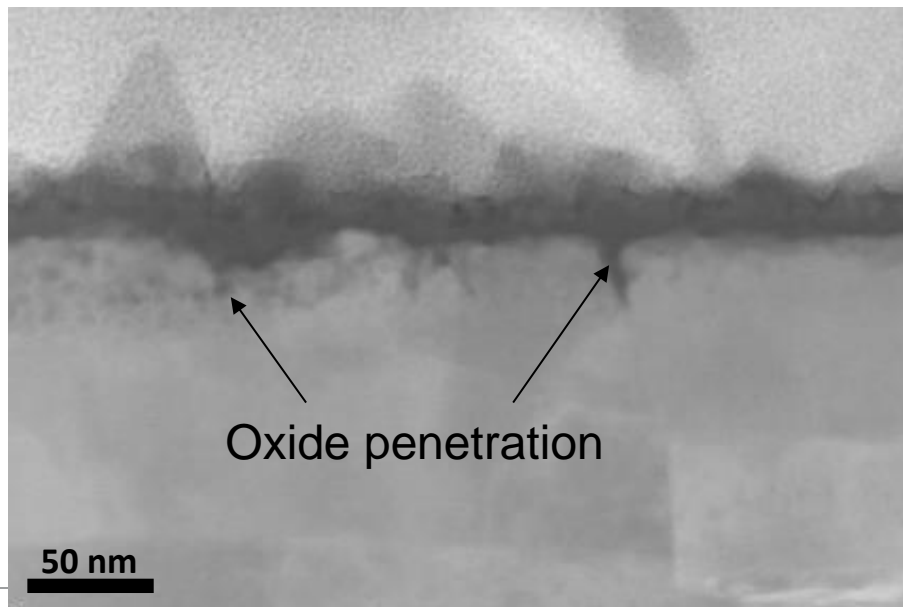
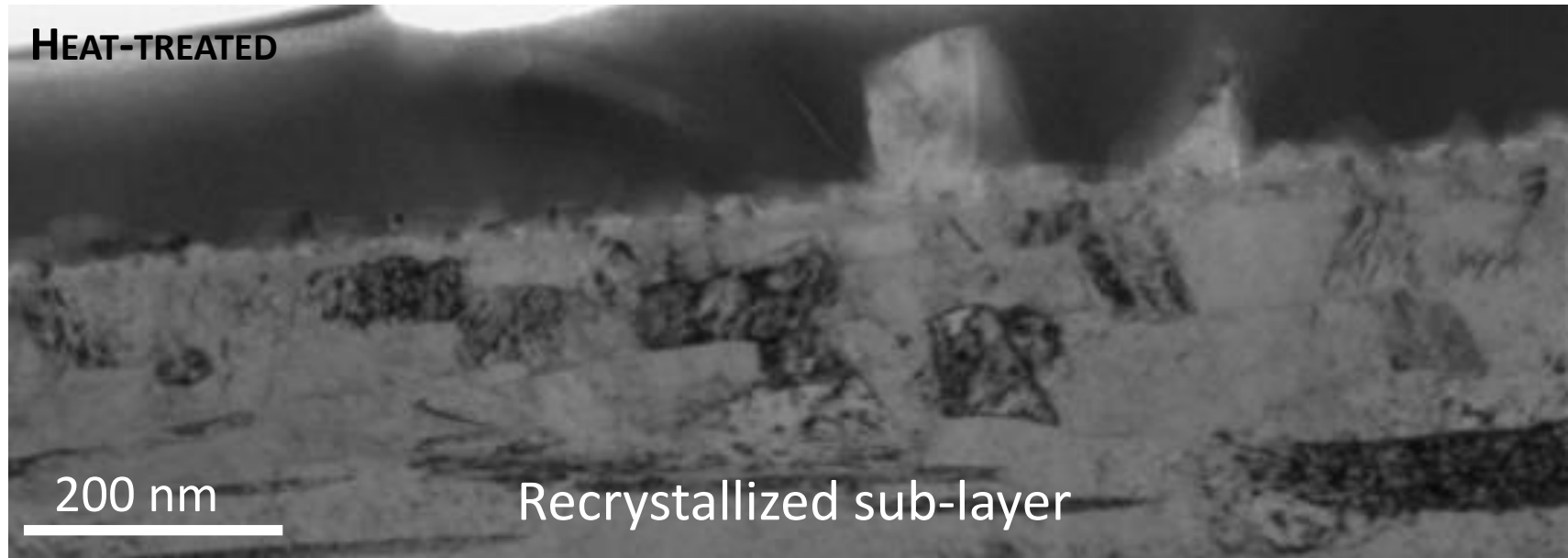


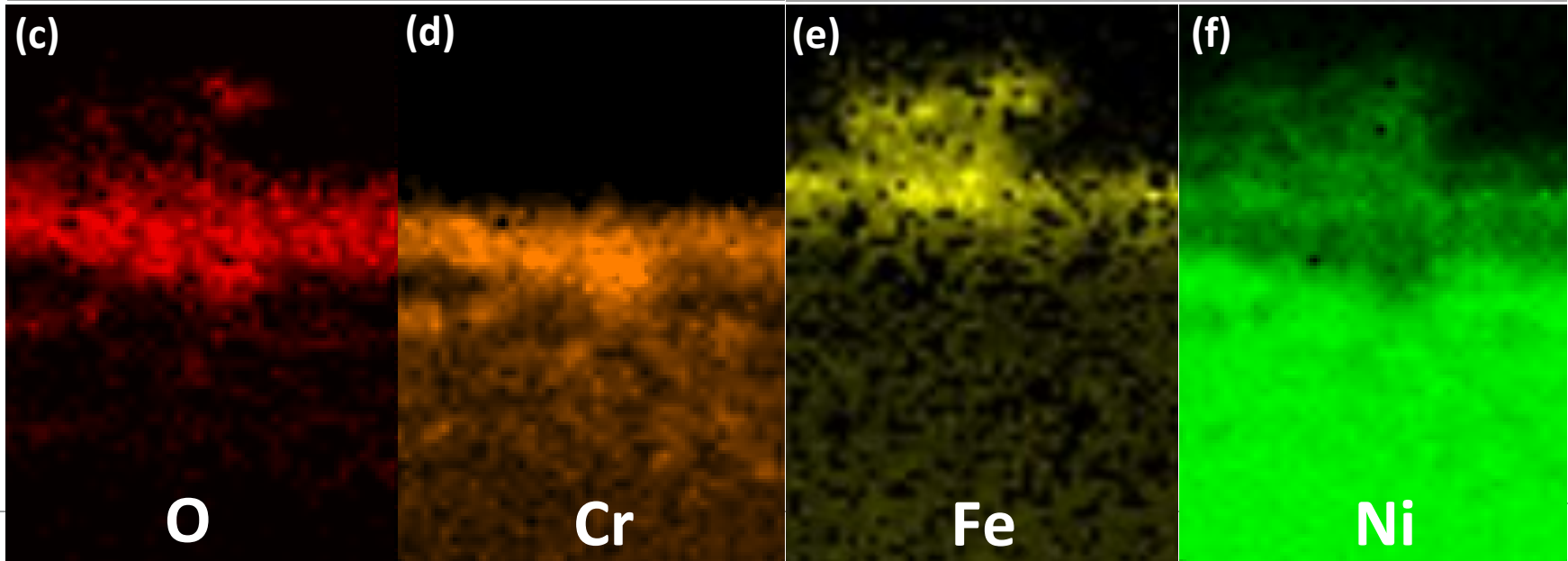
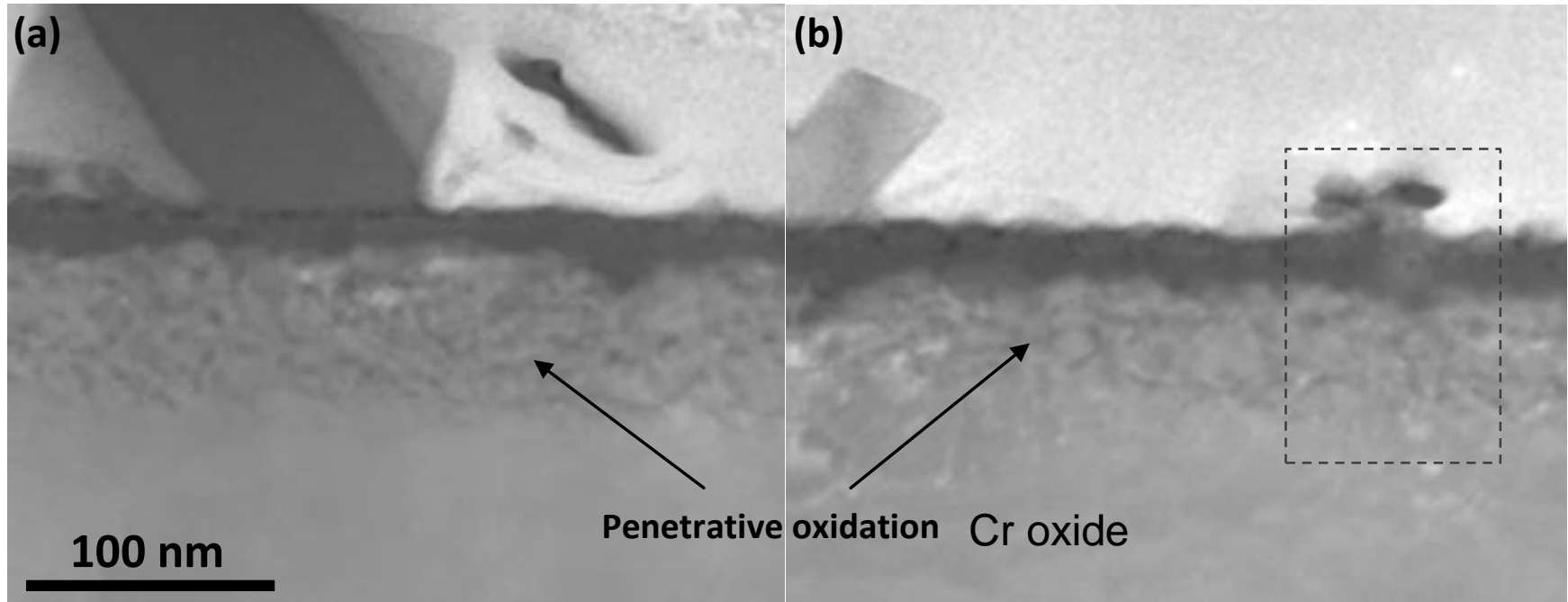
Outer layer
- NiFe_2O_4
- NiO
- filament

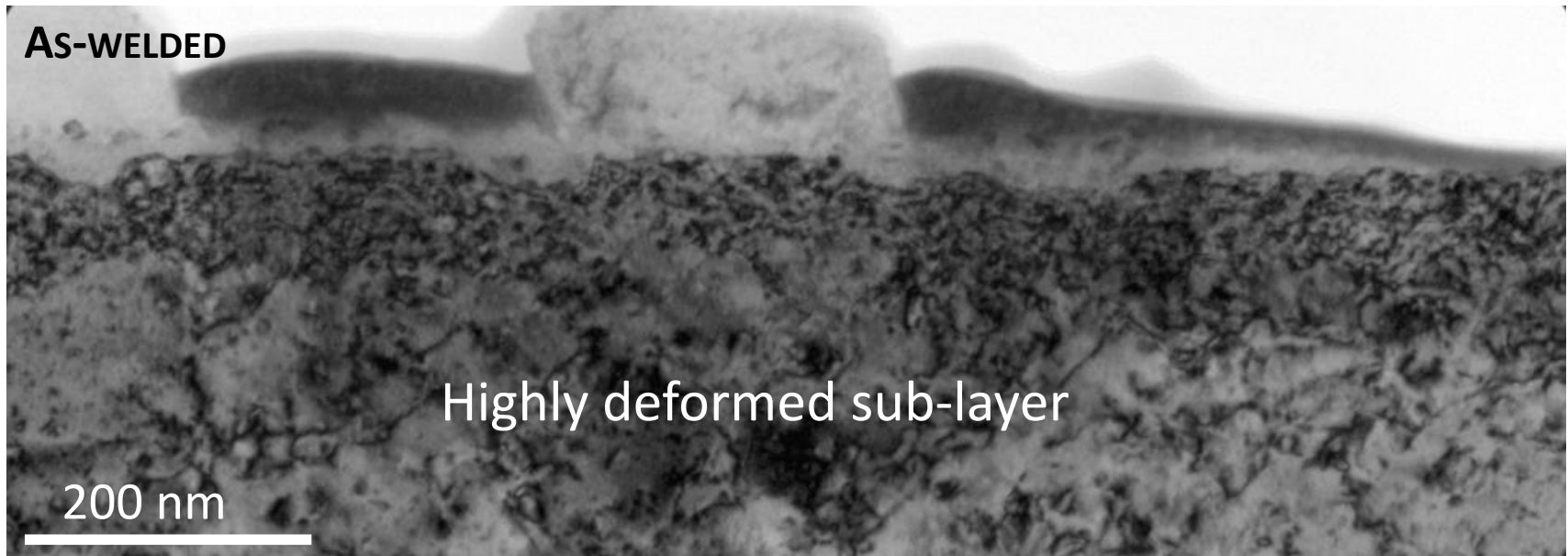
Inner layer
- NiCr_2O_4

Heat-treated samples

Primary water
Weld A – TT – 1500h



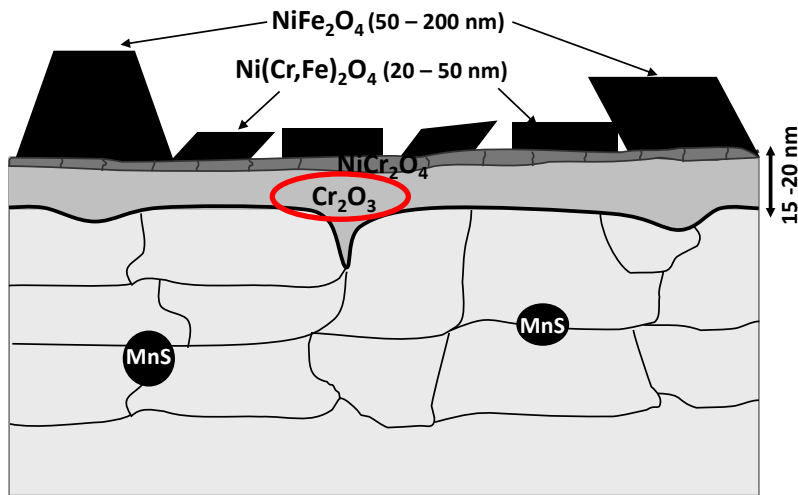




Summary

HYDROGENATED STEAM – 400°C

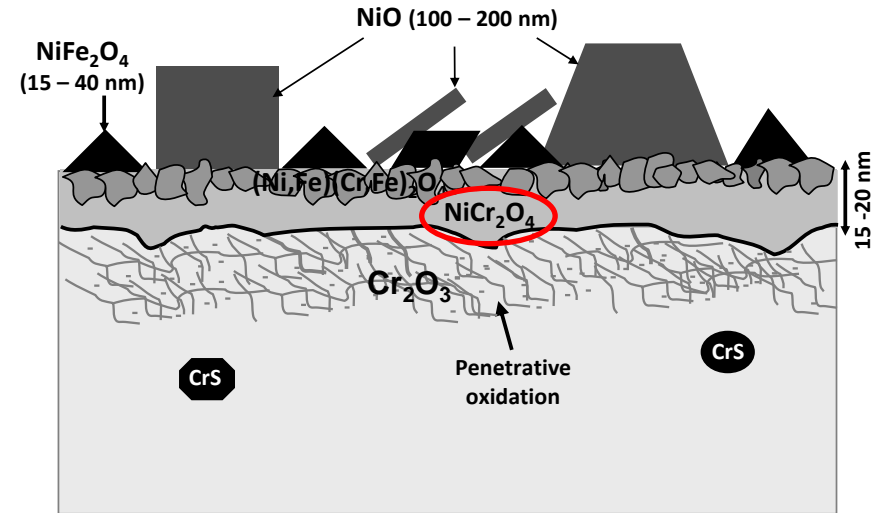
All samples



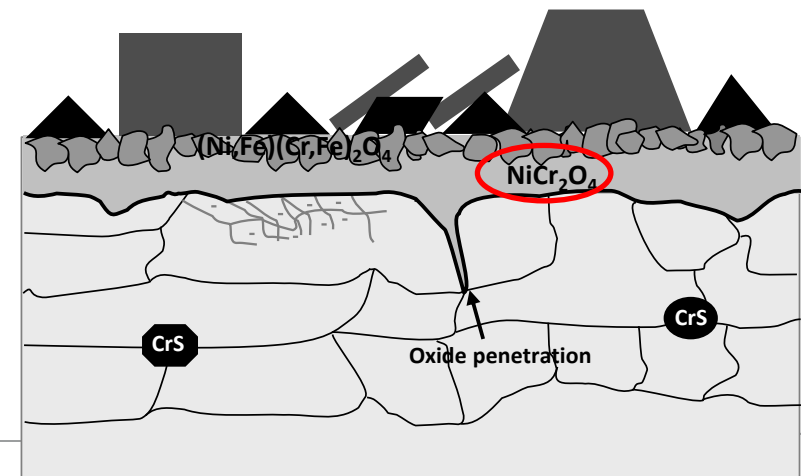
- Similar oxidation kinetics
- Duplex Cr-rich inner layer:
 - NiCr_2O_4 in primary water
 - Cr_2O_3 in hydrogenated steam
- Oxide penetrations

PRIMARY WATER – 340°C

As-welded



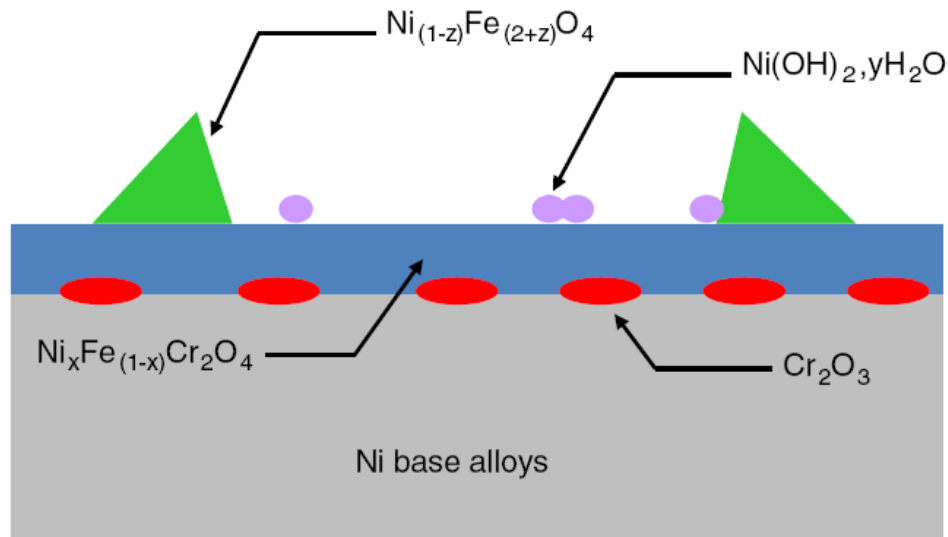
Heat-treated



Conclusions (1/2)

- Environment:

→ Surface oxide layer not strictly identical but consistent with literature data



Marchetti et al. (2015)

→ Similar oxidation tests performed on 304L SS show a difference in the oxidation kinetics but not in the oxide structure

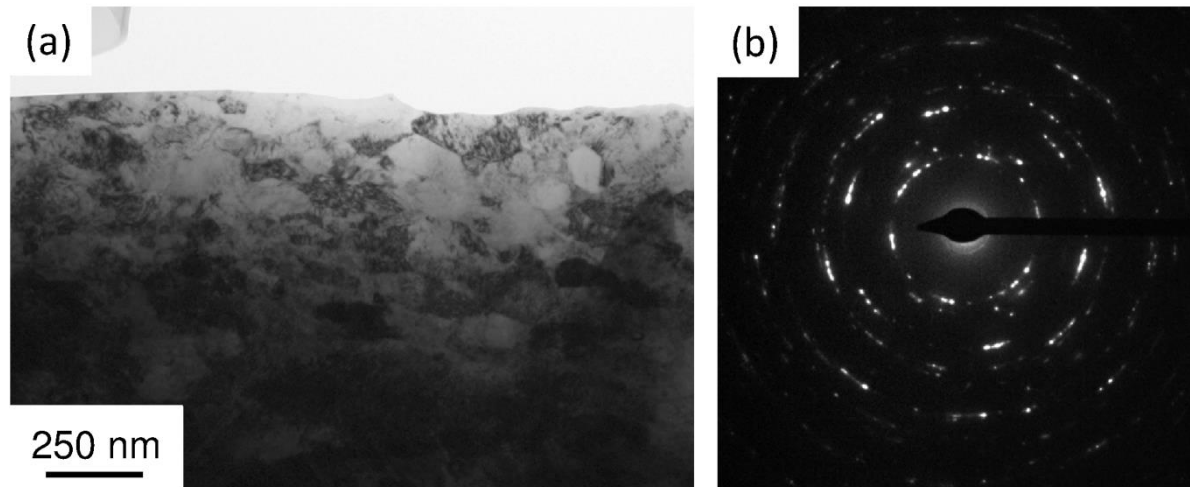
Cissé et al., JNM (2012)

Conclusions (2/2)

- Alloy microstructure:
 - For a given environment, no effect of weld composition, welding process or thermal treatment on the oxidation kinetics and oxide structure
 - Different sub-surface states: recrystallized or high density of dislocations
 - No effect on the continuous inner layer
 - But the morphology of oxide penetration strongly differs

Origin of the recrystallized layer?

As-prepared, non oxidized sample



→ Machining by EDM + grinding + mirror polish

Thank you for your attention