Oxidation Phenomena in Advanced High Strength Steels

IZA project: ZCO-62

GAP meeting, October 2015

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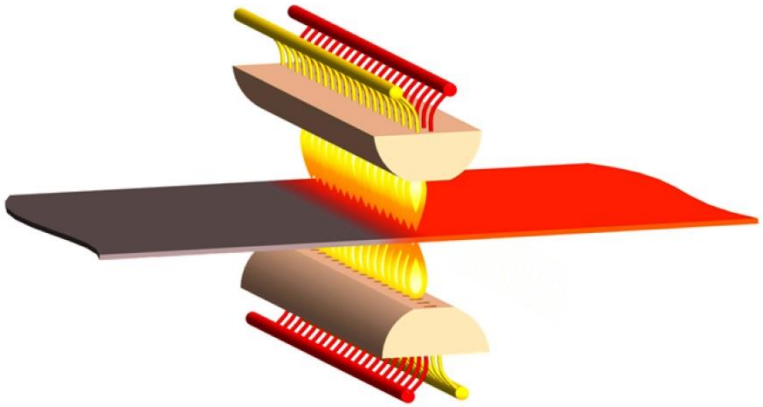
1.

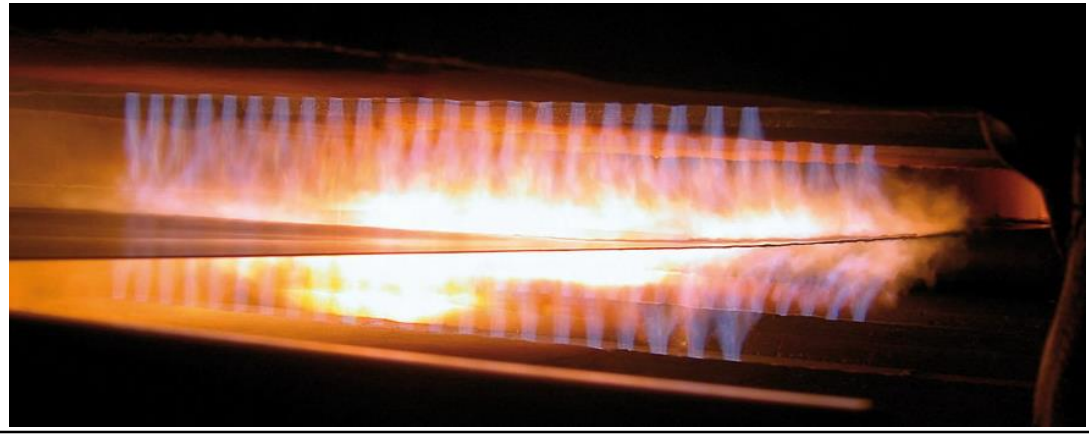
Introduction

DFI annealing of steel

Aim of REBOX DFI

- Cleaning of steel strip
- Efficient pre-heating





Research questions

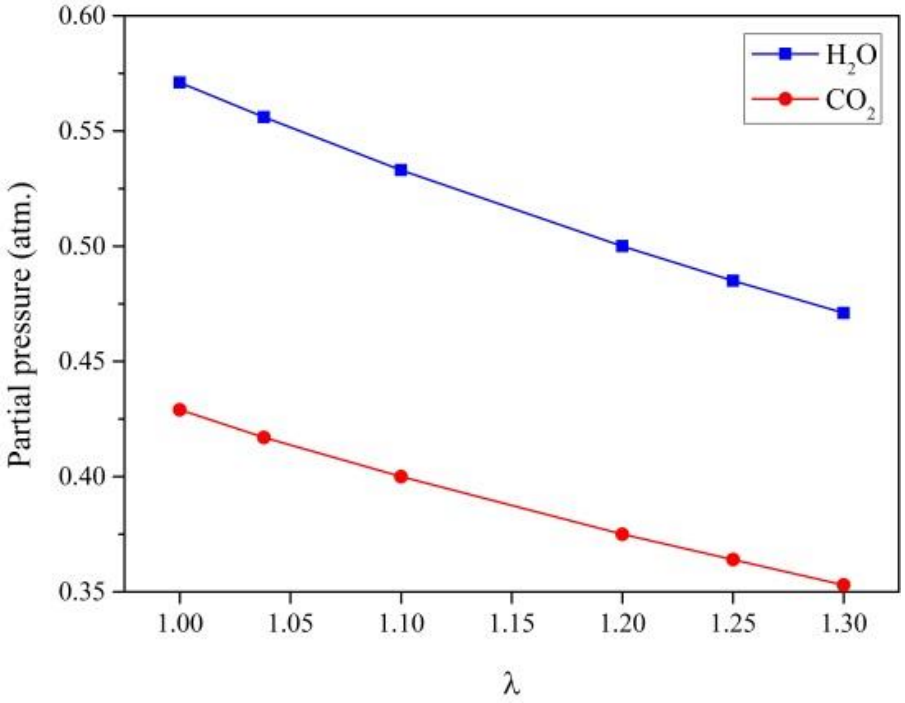
- How effective is the cleaning?
- How effective is the heating?
- Surface oxidation as a function of T and λ
- Internal / external oxidation of alloying elements as a function of T and λ

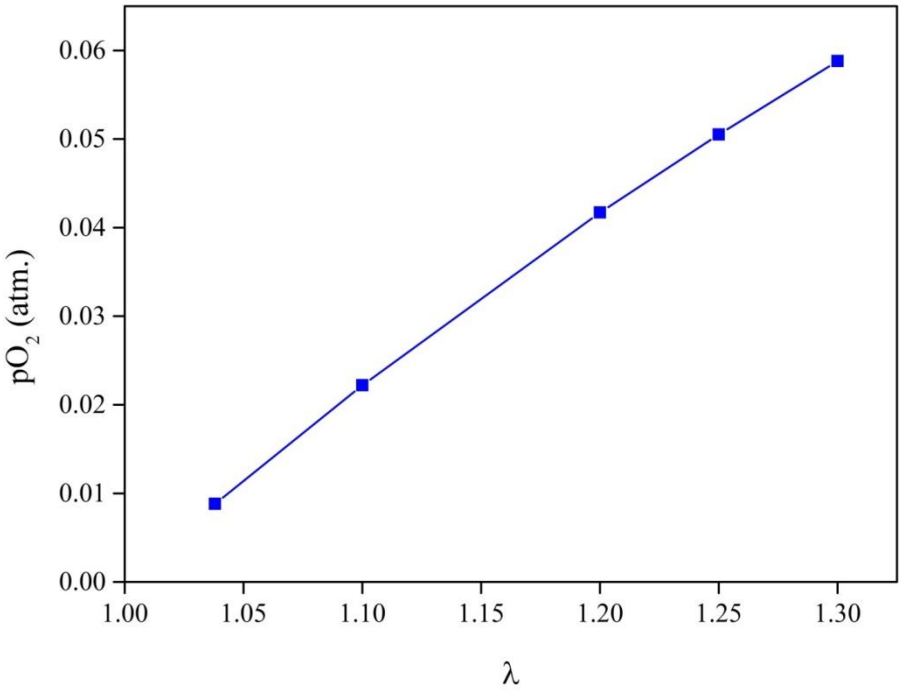
Choice of parameters

- $\lambda < 1$
  - low pO_2
  - significant formation of CO and H_2
- $\lambda > 1$
  - high pO_2
  - negligible amount of CO and H_2

Effect of lambda on gas composition

- Full combustion of propane [FactSage]

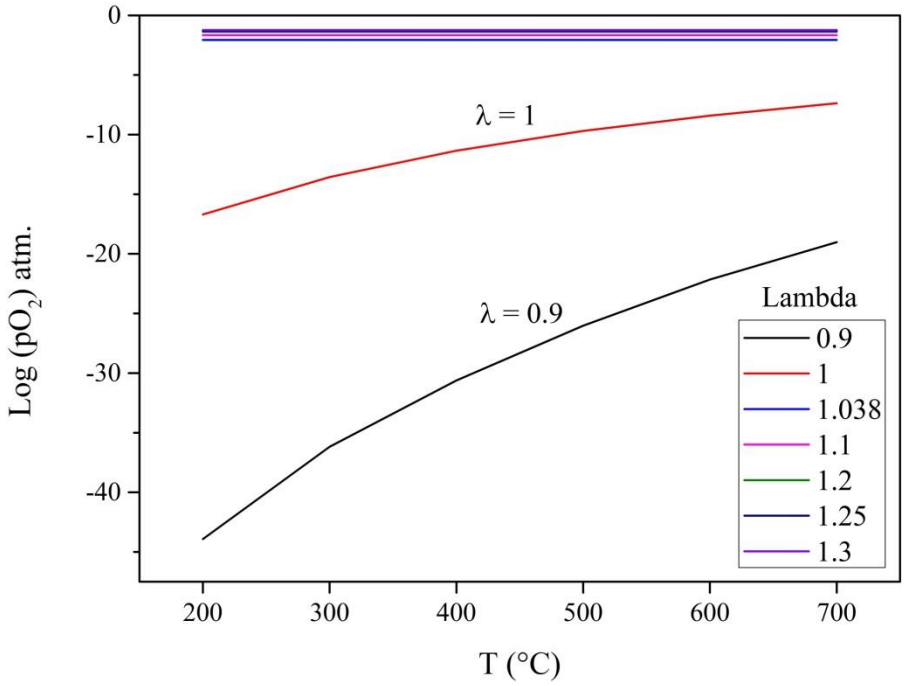


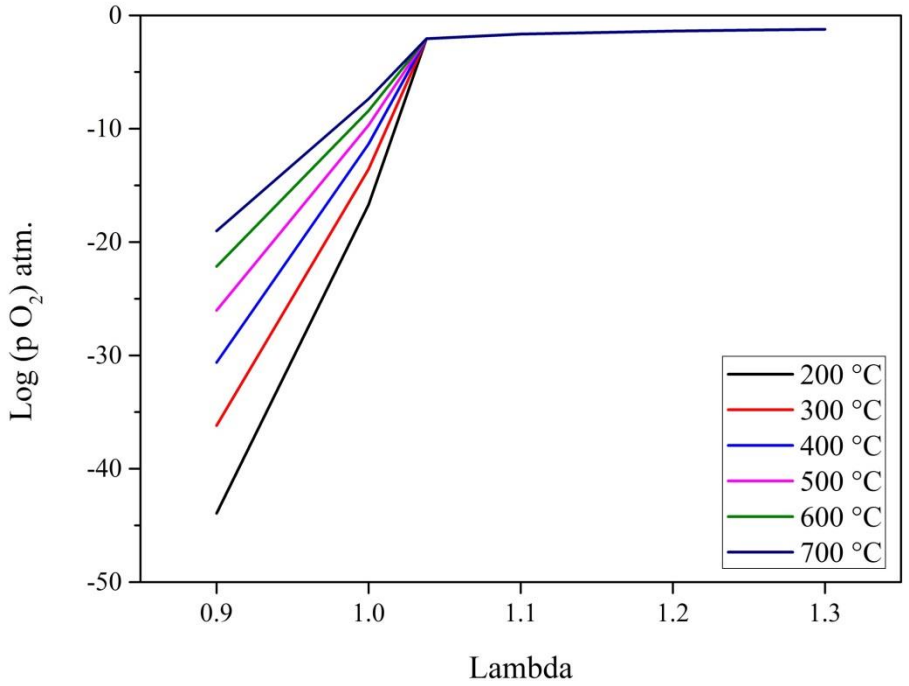


Gas composition of H_2O, CO_2 and O_2 are independent of T

Effect of T and λ on gas composition

- Combustion of propane [FactSage]

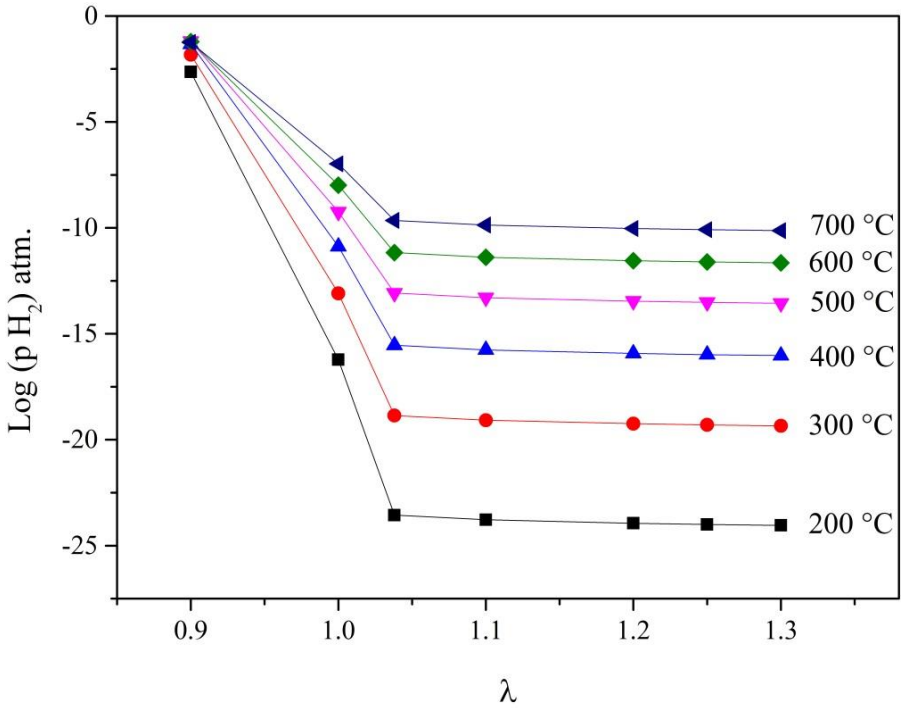


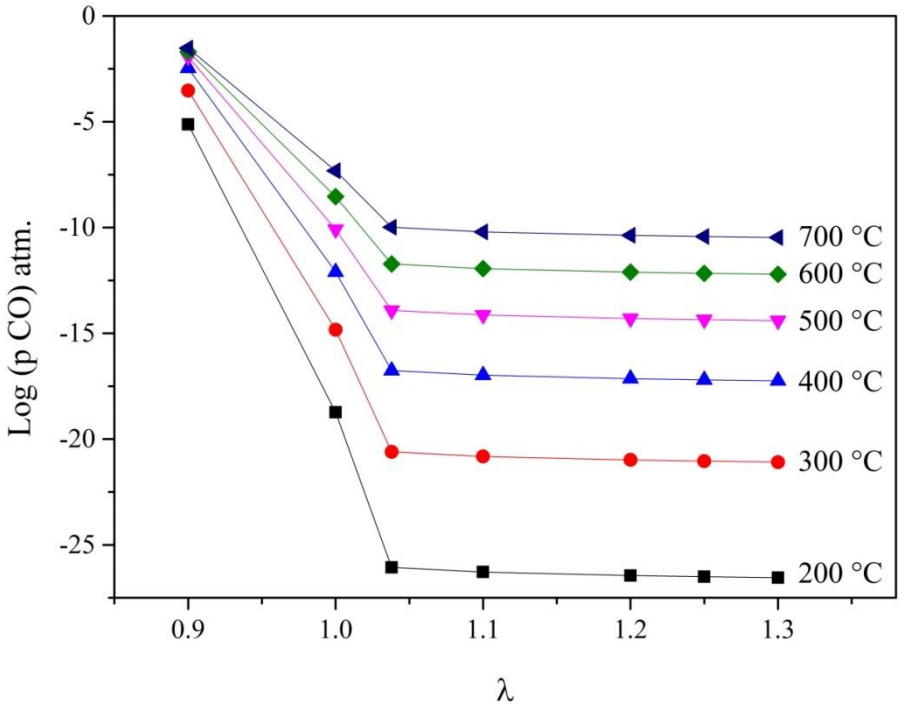


For λ≤1, gas composition depends on T

Effect of lambda on gas composition

- Combustion of propane [FactSage]





Gas composition of H_2 and CO depends on T

2.

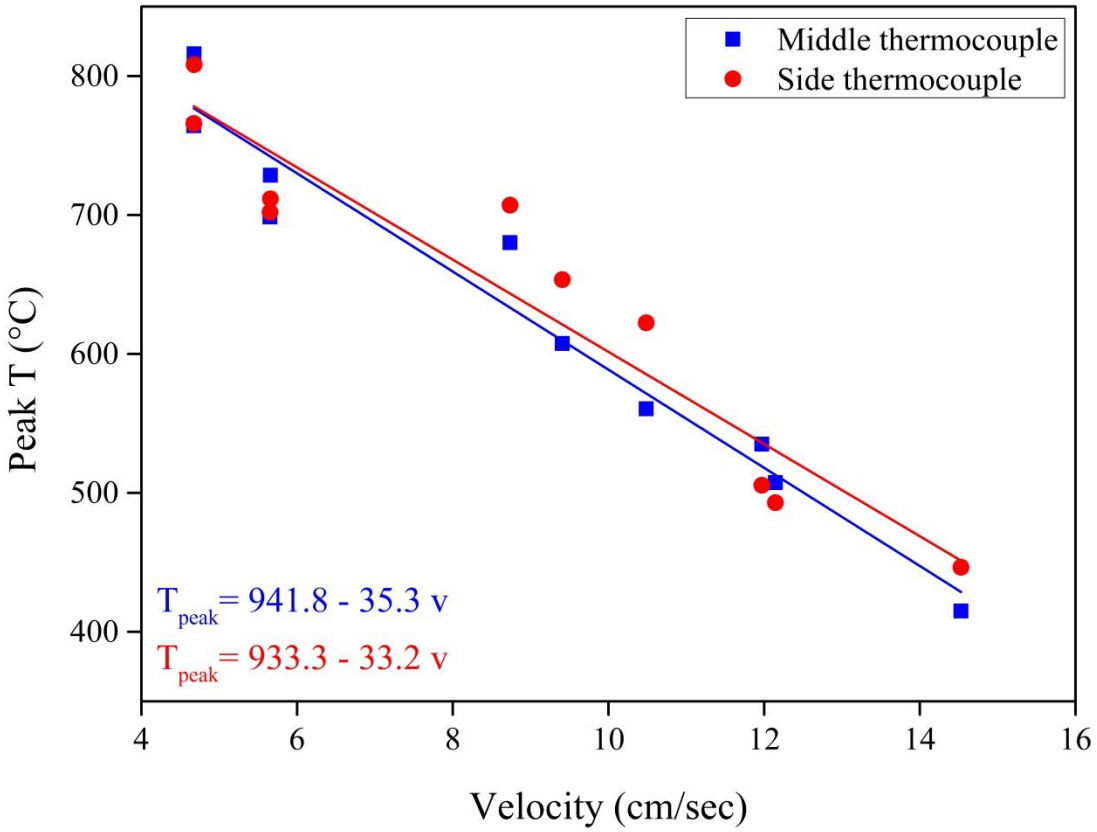
Experimental work

Chemical composition (wt%)

- DP 600 (grades A and B), provided by the TATA Steel Europe (IJmuiden, The Netherlands)
- 200 mm square plates

Grade	C	Mn	Si	Cr	Al
A	0.09	1.80	0.050	0.525	0.04
B	0.09	1.80	0.050	0.525	0.30

Peak T of steel plates and velocity



Excluding DA 5, DA 10, DB 4 and DB 5 data

T- measurement is not reliable

Expected oxide phases

- **Considering local equilibrium at steel surface**
- **Considering plate peak temperature**

	Sample code	T (° C)	Oxides
λ = 0.95	DA 5	423	Magnetite
	DA 11	535	Magnetite
	DA 6	608	Wüstite + Magnetite
	DA 4	816	Wüstite + Magnetite
λ = 1.00	DA 2	700	Wüstite + Magnetite + Hematite
	DA 1	729	Wüstite + Magnetite + Hematite

Wüstite for the first series and Wüstite/Hematite for the second series were not observed in XRD patterns (Bragg-Brentano geometry).

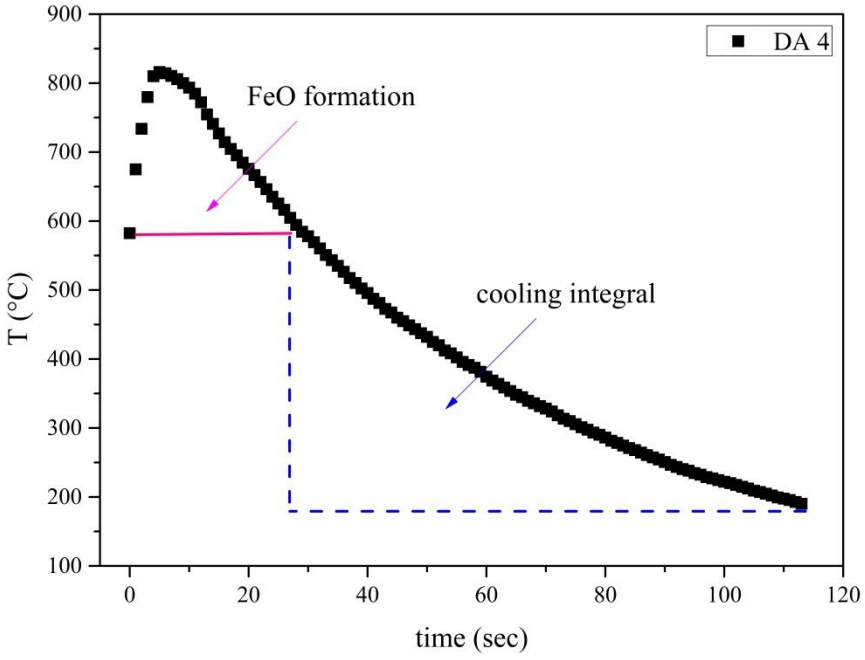
Grazing incidence XRD

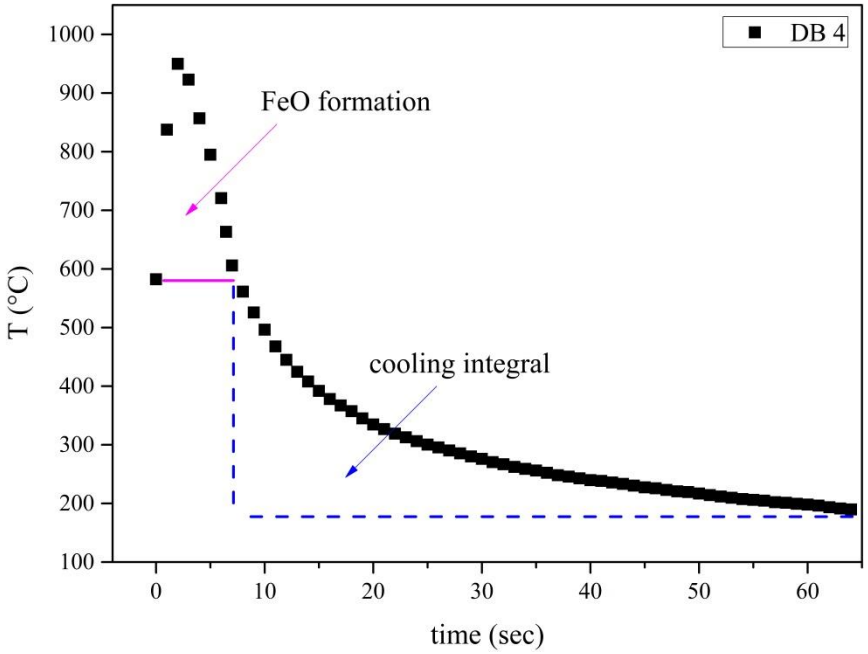
- λ = 0.95

Sample code	Plate peak T (°C)	Detected oxide phases	Expected oxide phases (thermodynamics)
DA 5	423	magnetite	magnetite
DA 6	608	magnetite	magnetite wüstite
DB 3	680	magnetite hematite	magnetite wüstite
DA 4	816	magnetite wüstite	magnetite wüstite
DB 4	950	magnetite	magnetite wüstite

DA 4 (816 °C) and DB 4 (950 °C)

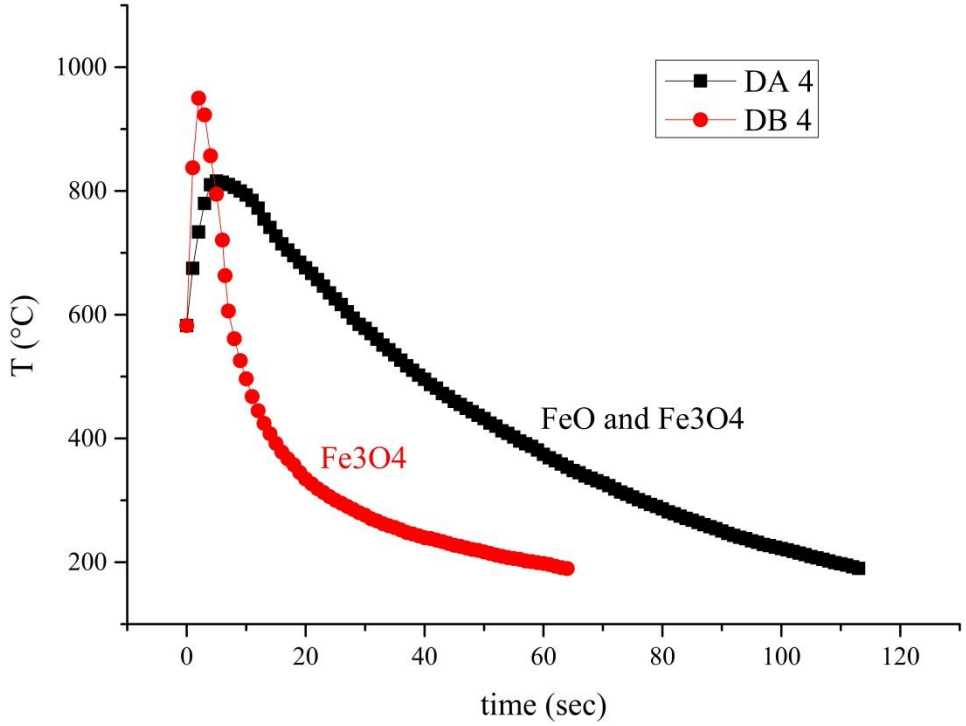
- Although the cooling of DA 4 is slower than for DB 4, T-t integral for formation of FeO for DA 4 is much larger than for DB 4. Hence, FeO is observed only for DA 4.





DA 4 and DB 4 (cont.)

- Although the cooling of DA 4 is slower than for DB 4, T-t integral for formation of FeO for DA 4 is much larger than for DB 4. Hence, FeO is observed only for DA 4.



Summary of XRD results

- Bragg-Brentano geometry
  - Large contribution of steel substrate
  - Fe and magnetite were detected
  - Wüstite was detected only for sample DA 4 (816 ºC)
    - XRD on formed oxide flakes

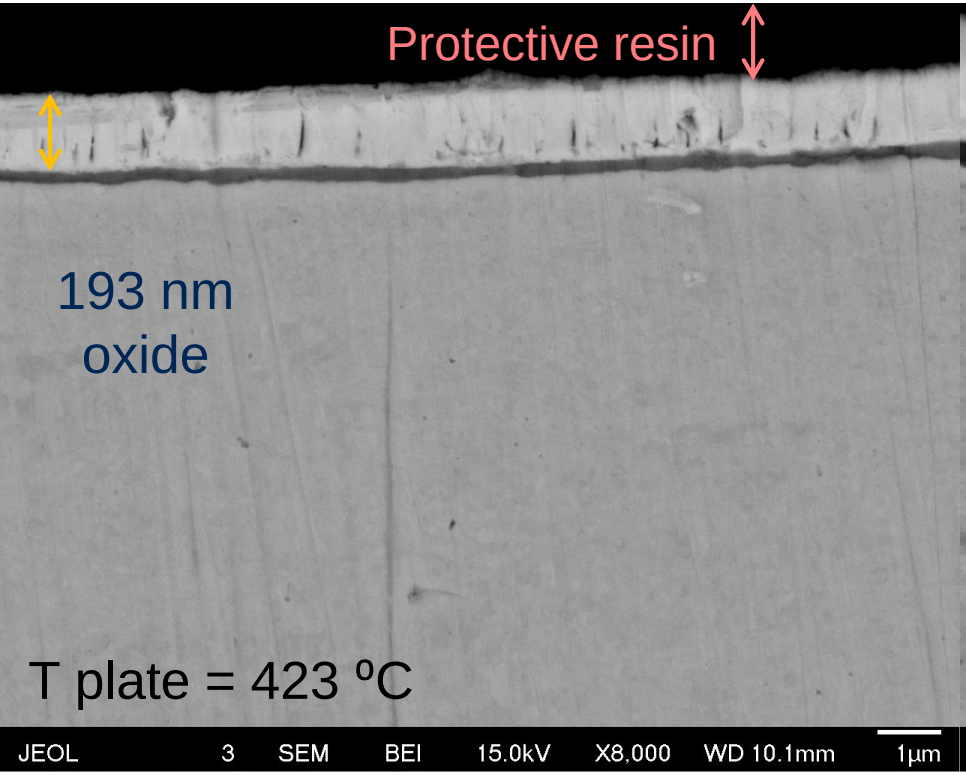
- Grazing incidence XRD (θ = 3 º, analyzing depth 1.3 µm)
  - To minimize contribution of Fe matrix
  - Detection of surface phase
  - Fe and magnetite were detected (for all samples)
  - Wüstite and hematite were also detected for DA 4 and DB 3, respectively

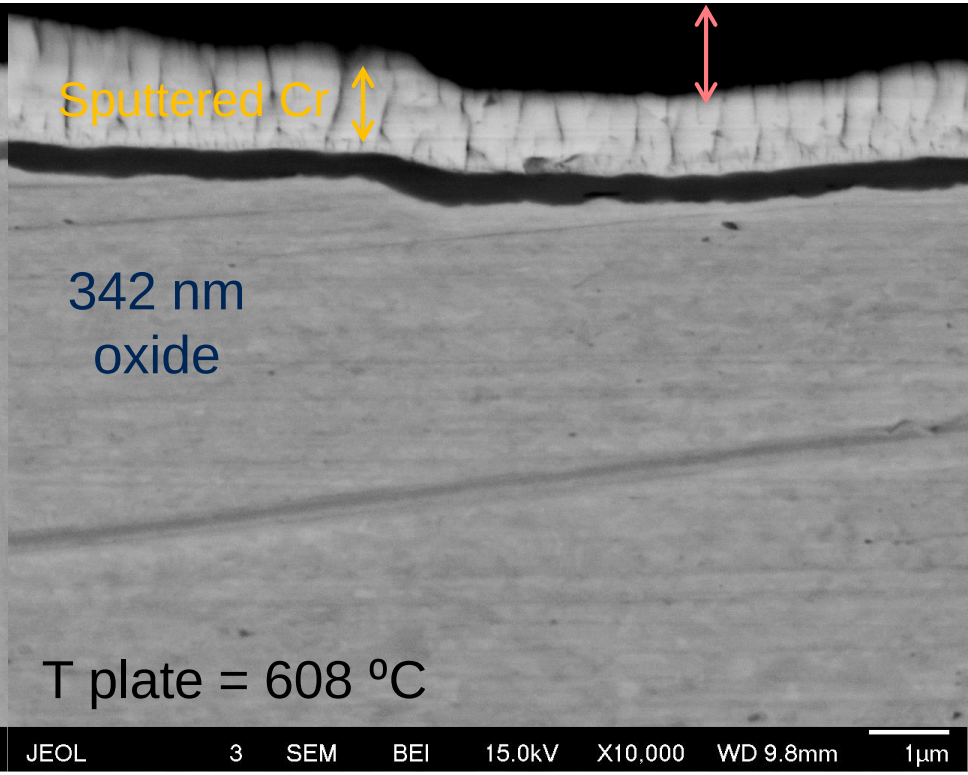
Summary of XRD results (cont.)

- FeO is expected to form above 570 ºC
  - however, upon cooling FeO can be transformed into Fe_3O_4
- Amount of initially formed FeO phase may play a role
  - see slides number 14 and 15

SEM images of cross-sections

- λ = 0.95
- Uniform oxide layer

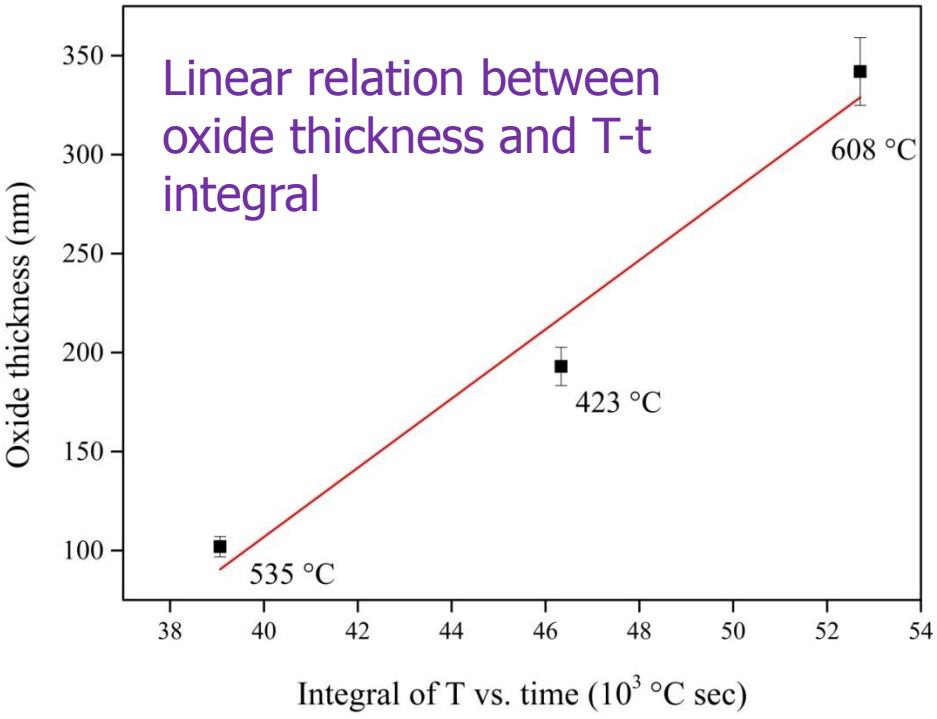




Oxide thickness vs T-t integral

- Oxide thickness was measured with SEM from cross-section images

Sample code	λ	Plate peak T (° C)	Oxide thickness (nm)
DA 5	0.95	423	193 ± 22
DA 11	0.95	535	102 ± 16
DA 6	0.95	608	342 ± 57



Effect of λ on oxide thickness

- Significant increase in oxygen partial pressure by increasing the λ

Plate peak T (° C)	Oxide thickness (nm)	Lambda
423	193 ± 22	0.95
535	102 ± 16	0.95
608	342 ± 57	0.95
816	>> 204	0.95
699	1.24 ± 0.05 µm	1
729	1.50 ± 0.06 µm	1

XPS results

- Surface chemistry of oxidized samples
- Binding energies in eV

Sample	Plate peak T (° C)	Fe $2p_{3/2}$	O 1s (oxide) O 1s (hydroxide)	Mn $2p_{3/2}$	Mn (at.%)	Al Cr Si
DB 2	415	709.1	530.0 531.4	640.7	0.9	n.d.
DB 1	507	709.1	530.0 531.4	640.2	5.7	n.d.
DB 4	950	709.2	530.1 531.5	640.4	3.2	n.d.

Mn^{2+} is detected (formation of mixed Fe, Mn oxide)
Al, Cr and Si were not detected at the surface

3.

Future research

Discussion

- Proposed new experimental matrix for DFI process

	Plate T (°C)	Lambda
Linde Gas	300, 400, 500, 600 and 700	0.9, 1.0, 1.038 and 1.25
CMI	200 and 300	0.9 and 1.0
Andritz		0.9
Bao Steel	400, 500, 600, 700 and 750	0.9 – 1.1
ThyssenKrupp	400, 500, 600 and 700	0.9, 1.0, 1.1, 1.2 and 1.3

Discussion (cont.)

- 16 experiments in total (doable)

		T (°C)					
		200	300	400	500	600	700
λ	0.9						
	1.0						
	1.038						
	1.1						
	1.2						
	1.25						
	1.3						