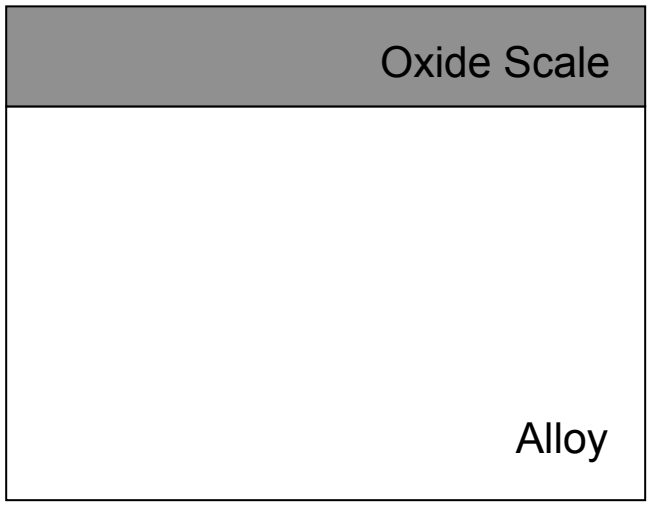
高温酸化アルミナ皮膜の生成･相変態におよぼす種々の因子

―初期酸化皮膜から安定アルミナ皮膜への遷移―

林　重成
東京工業大学大学院理工学研究科
材料工学専攻

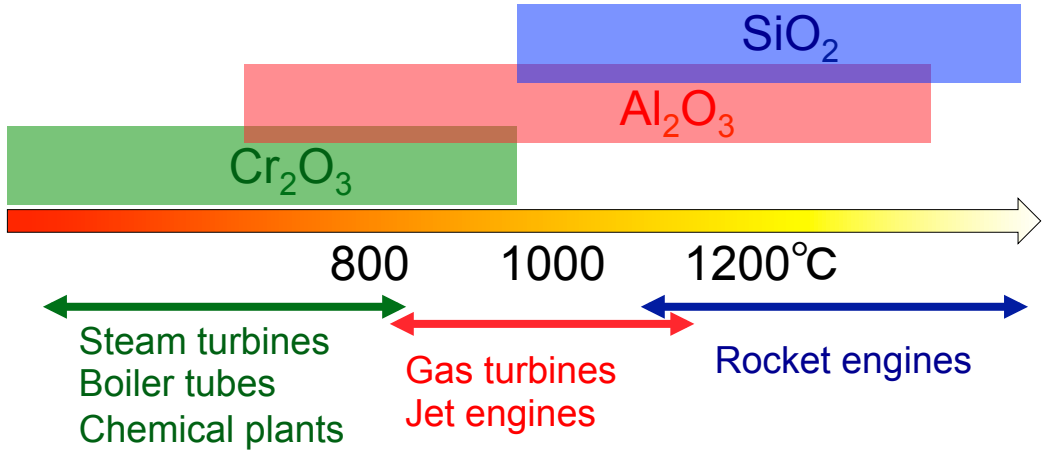
Protection of Heat-resistant Alloys Against High-Temperature Oxidation and Corrosion

Higher Temperature
Oxidizing, Corrosive atmospheres

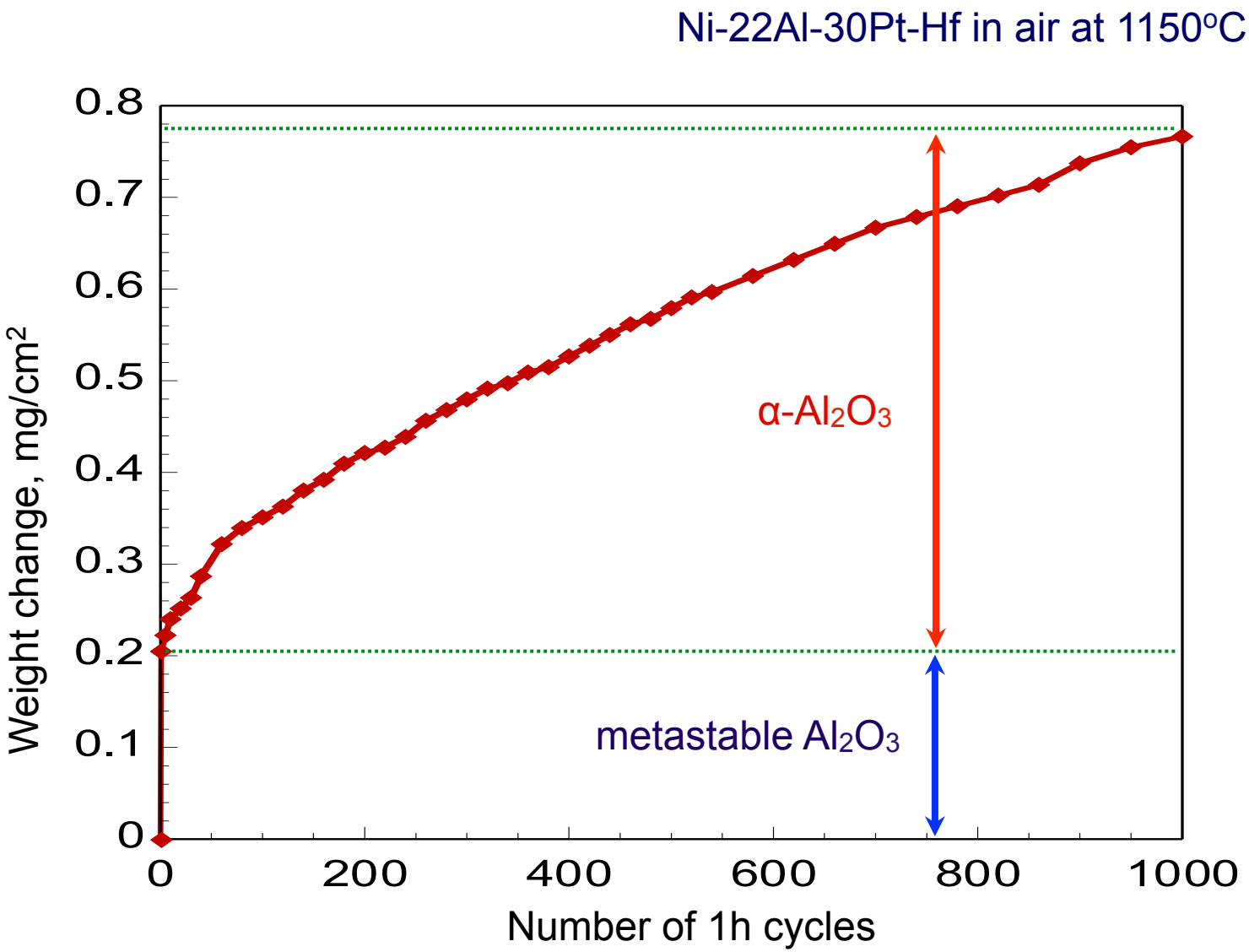


1. Compact, Higher thermo-dynamical Stability
2. Good adhesion to substrate
3. Rapid formation, maintained for longer time

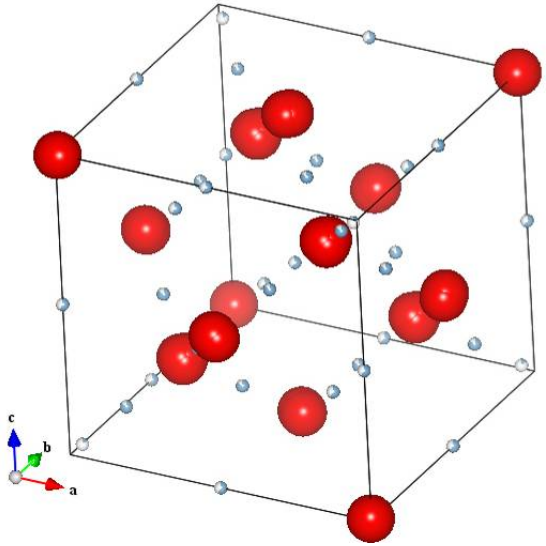
Cr_2O_3, Al_2O_3, and SiO_2



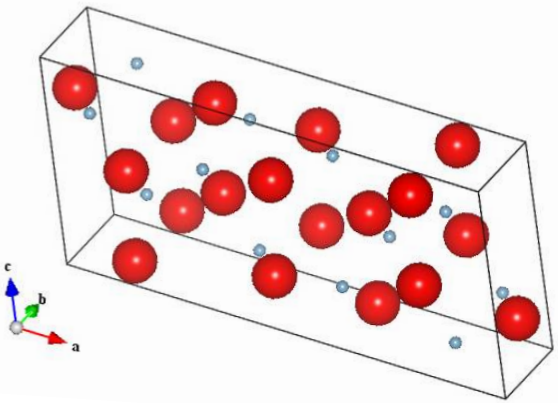
Growth of Metastable and α-Al_2O_3 Scale



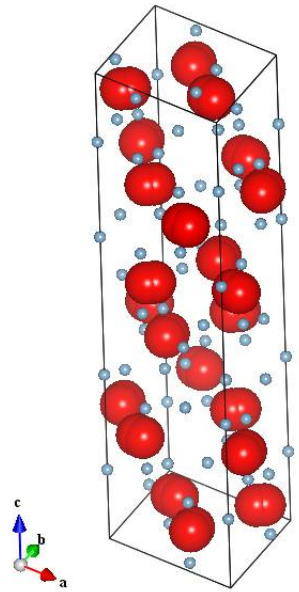
Typical Forms Thermally Grown Alumina



γ-Al_2O_3
(Cubic)



θ-Al_2O_3
(Monoclinic)



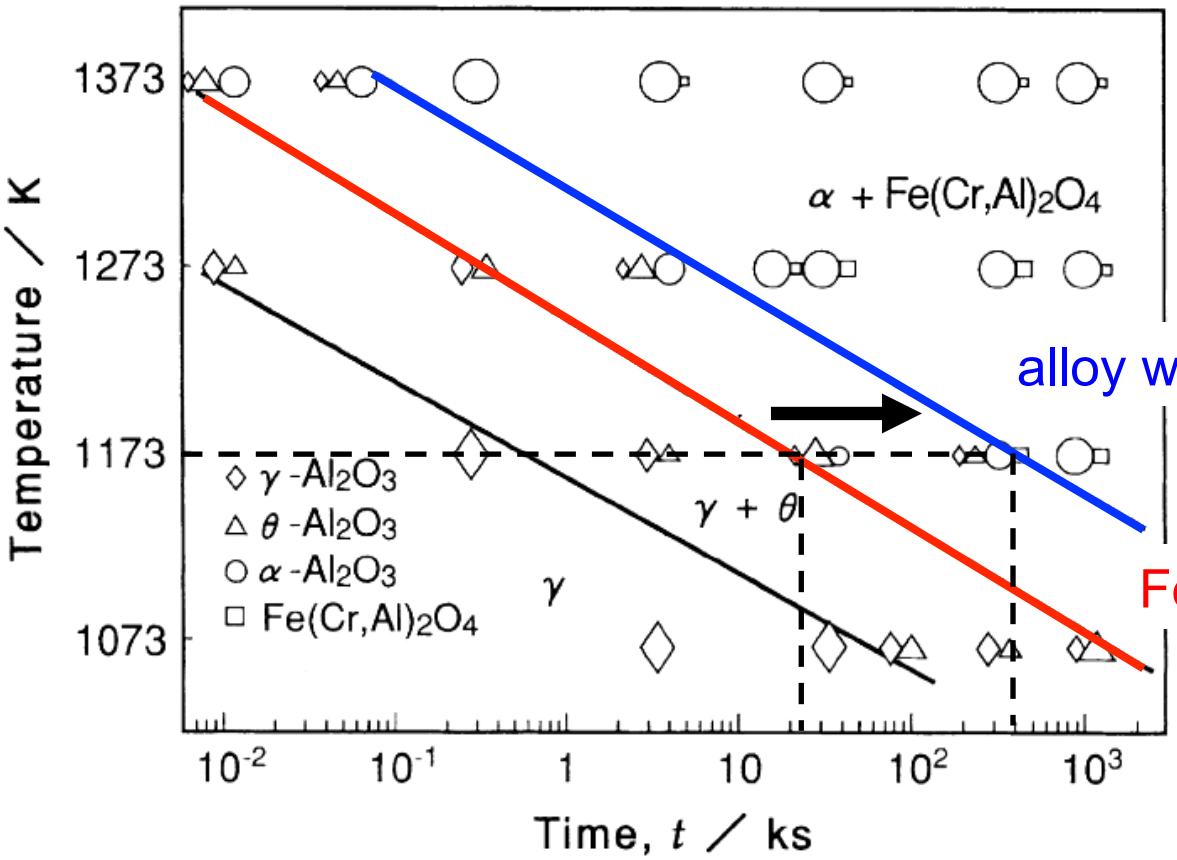
α-Al_2O_3
(Corundum)

Alloy composition

Atmosphere

Temperature

TTT Diagram of Thermally Grown Alumina

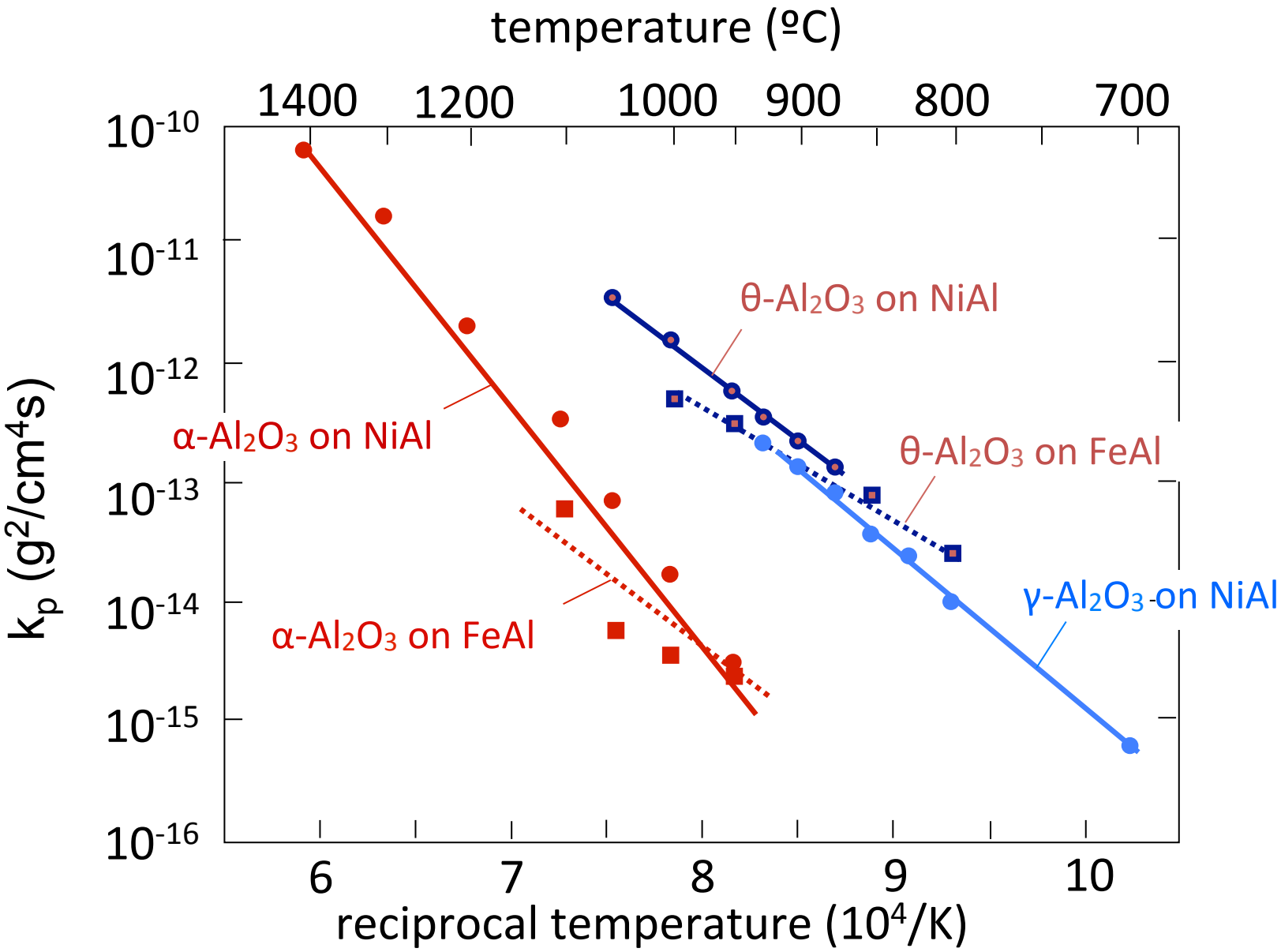


alloy with Al deposition

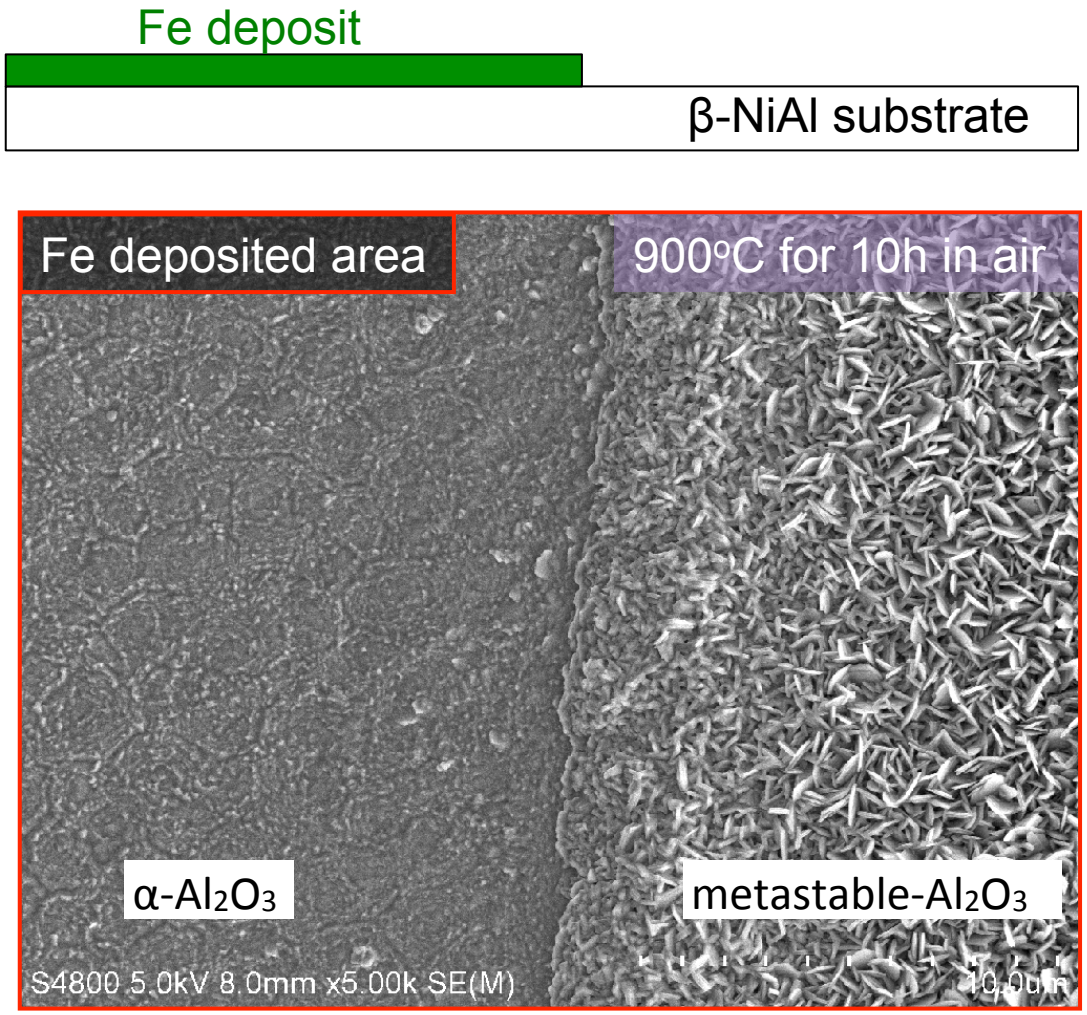
FeCrAl alloy

S. Taniguchi and A. Andoh, *Oxid. Met.*, 58, (2002), 545.

Growth rates of metastable and α-Al_2O_3 scales

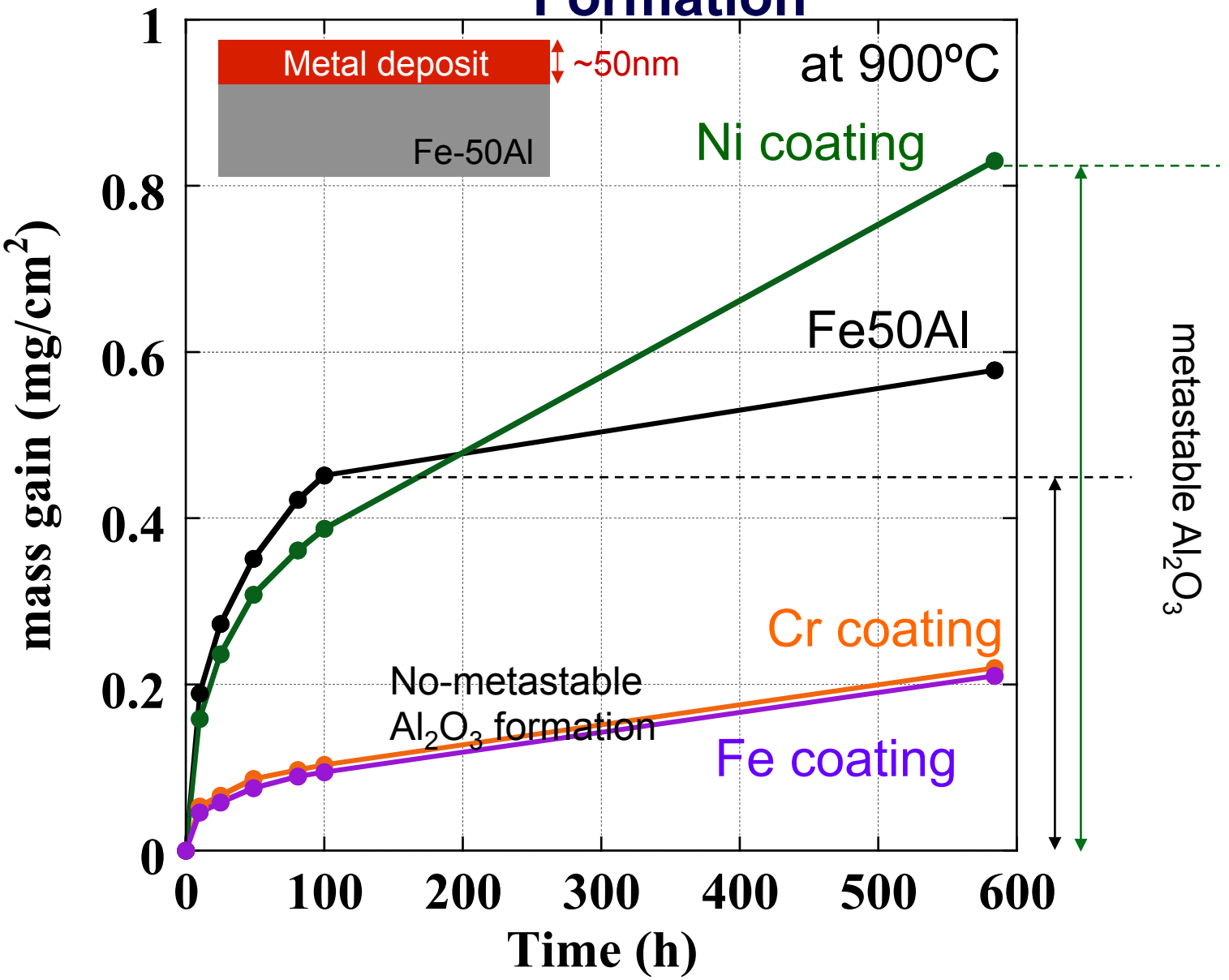


Effect(s) of Fe Deposit on the Phase Transformation to α-Al_2O_3



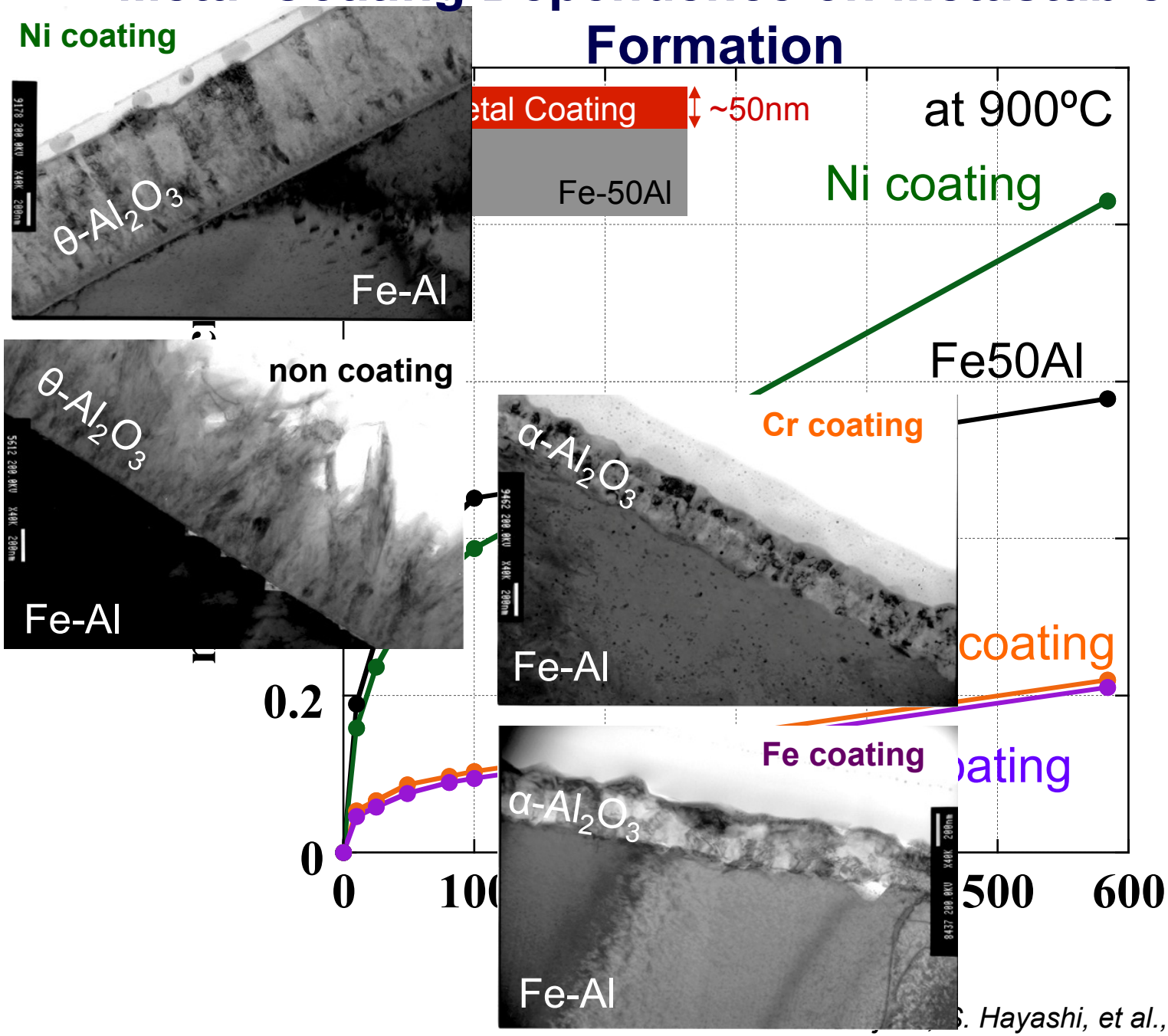
T. Nishimoto, T. Narita, JIM annual meeting, (2007).

Metal Coating Dependence on Metastable Al_2O_3 Formation



Y. Kitajima, S. Hayashi, et al., Oxid. Met., (2010)

Metal Coating Dependence on Metastable Al_2O_3 Formation



S. Hayashi, et al., Oxid. Met., (2010)

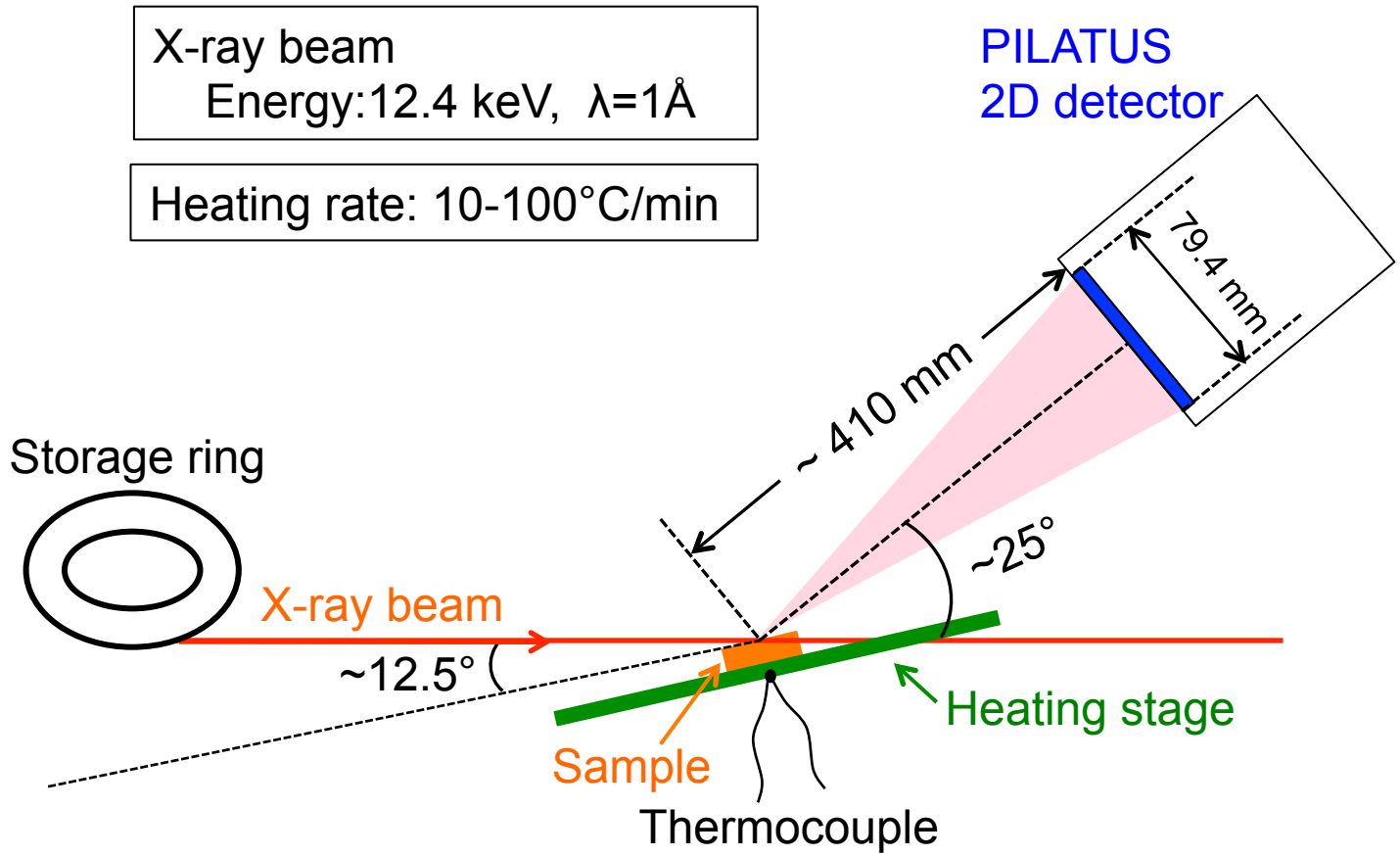
Purpose of the Study

Clarify the effect of various elements on the transformation behavior of Al_2O_3 scale during HT oxidation by in-situ HT X-ray diffraction study by means of synchrotron radiation.

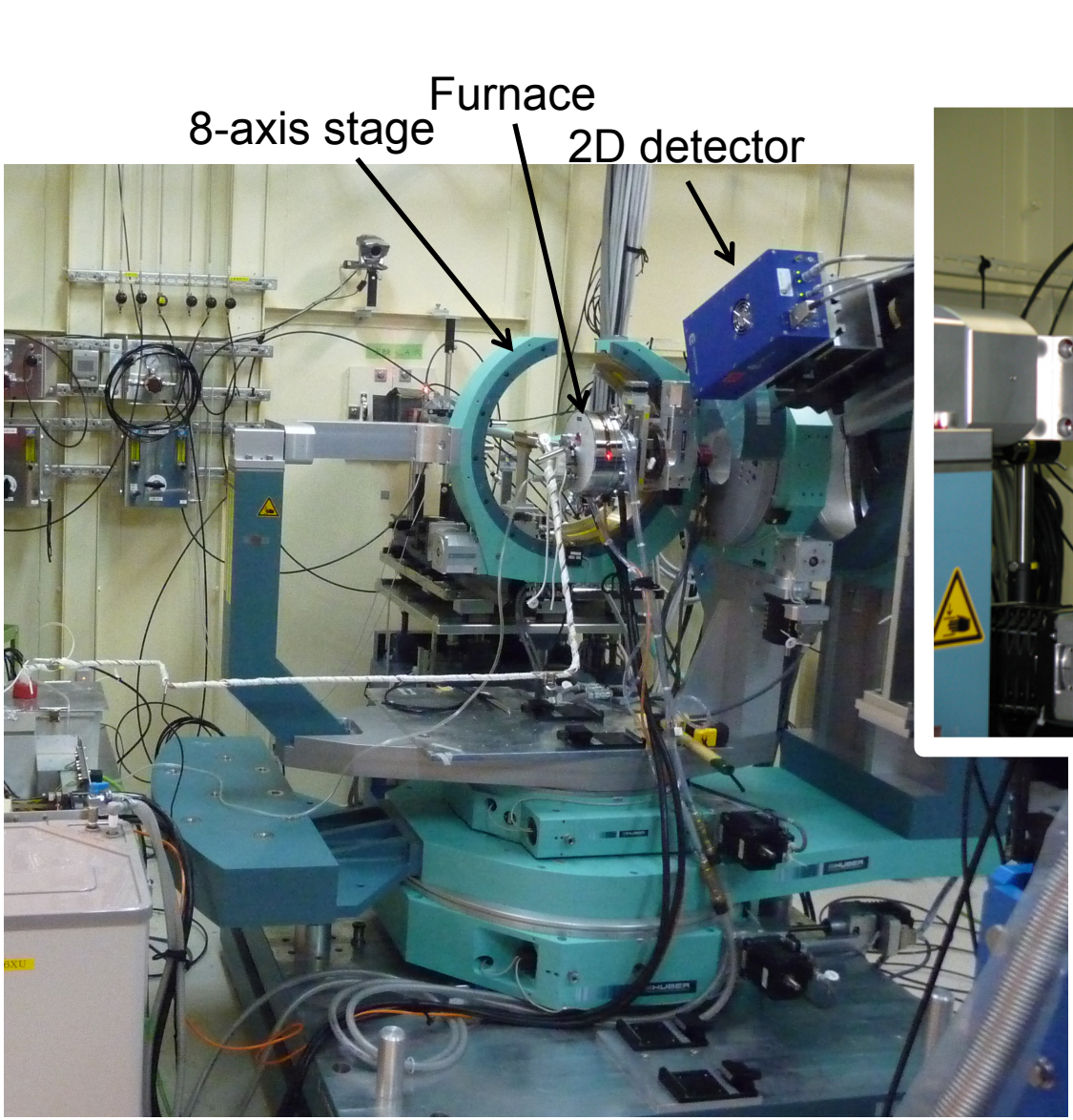
Experimental Setup for *In-situ* Measurement

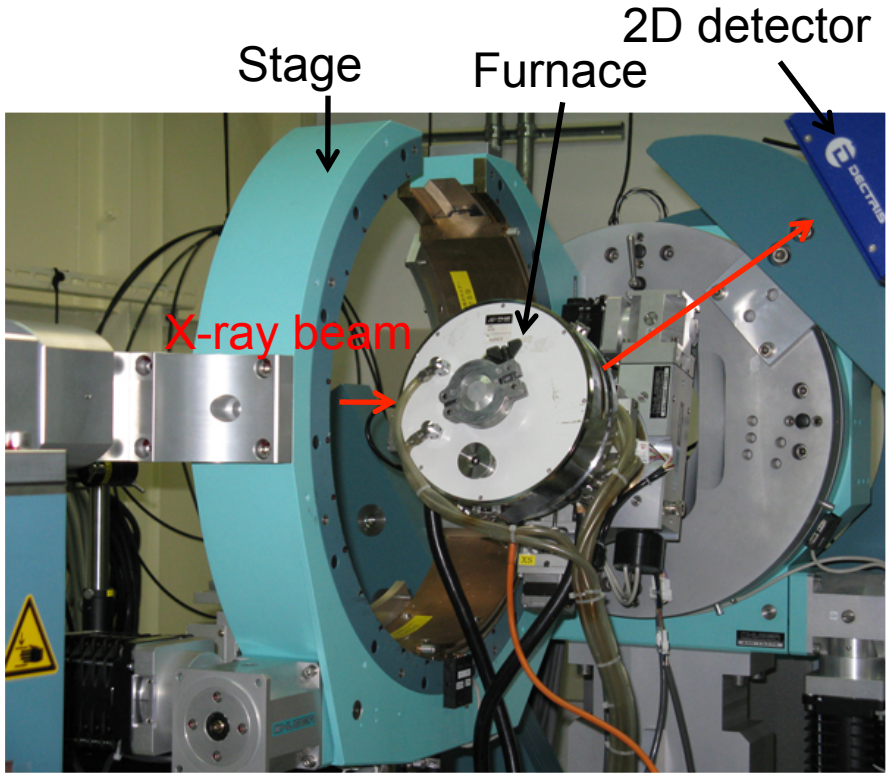
X-ray beam
Energy:12.4 keV, λ=1Å

Heating rate: 10-100°C/min



Experimental Setup for *In-situ* Measurement





Experimental Procedures

Effect of Fe on the Transformation of Al2O3 Scale

Alloys: Fe-45~52at%Al (FeAl)

Coatings: Fe ~100nm (PVD)

Oxidation: in air, air + 7.6H_2O

in lowP_{O2} = 1.8 x 10^{-13} atm (Ar-0.9H_2-7.6H_2O)

(FeO/Fe_3O_4, 1.2 x 10^{-12} atm)

at 1000 ~ 1100°C

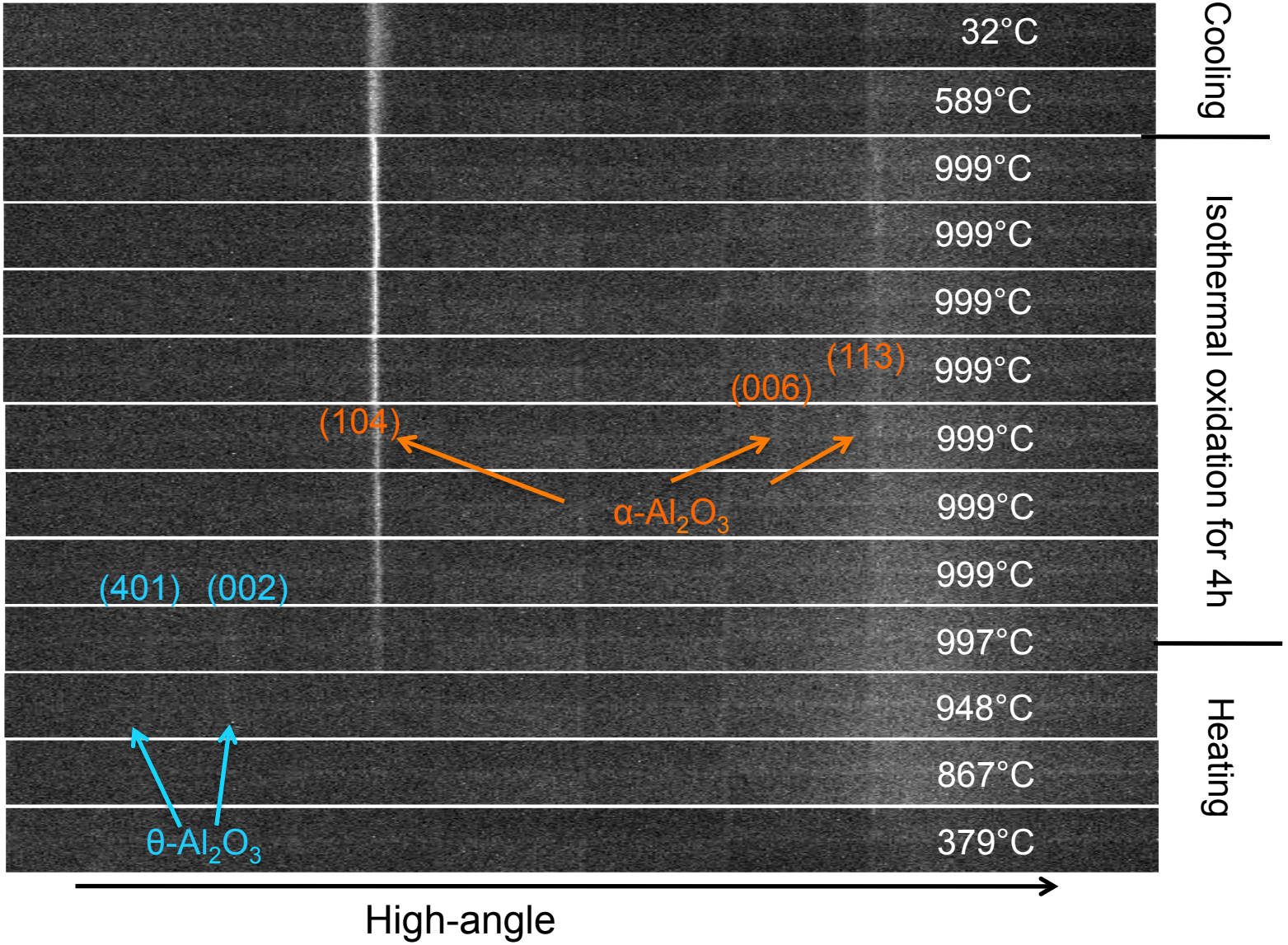
Heating and cooling rate : 50°C/min for heating

about 300°C/min for cooling

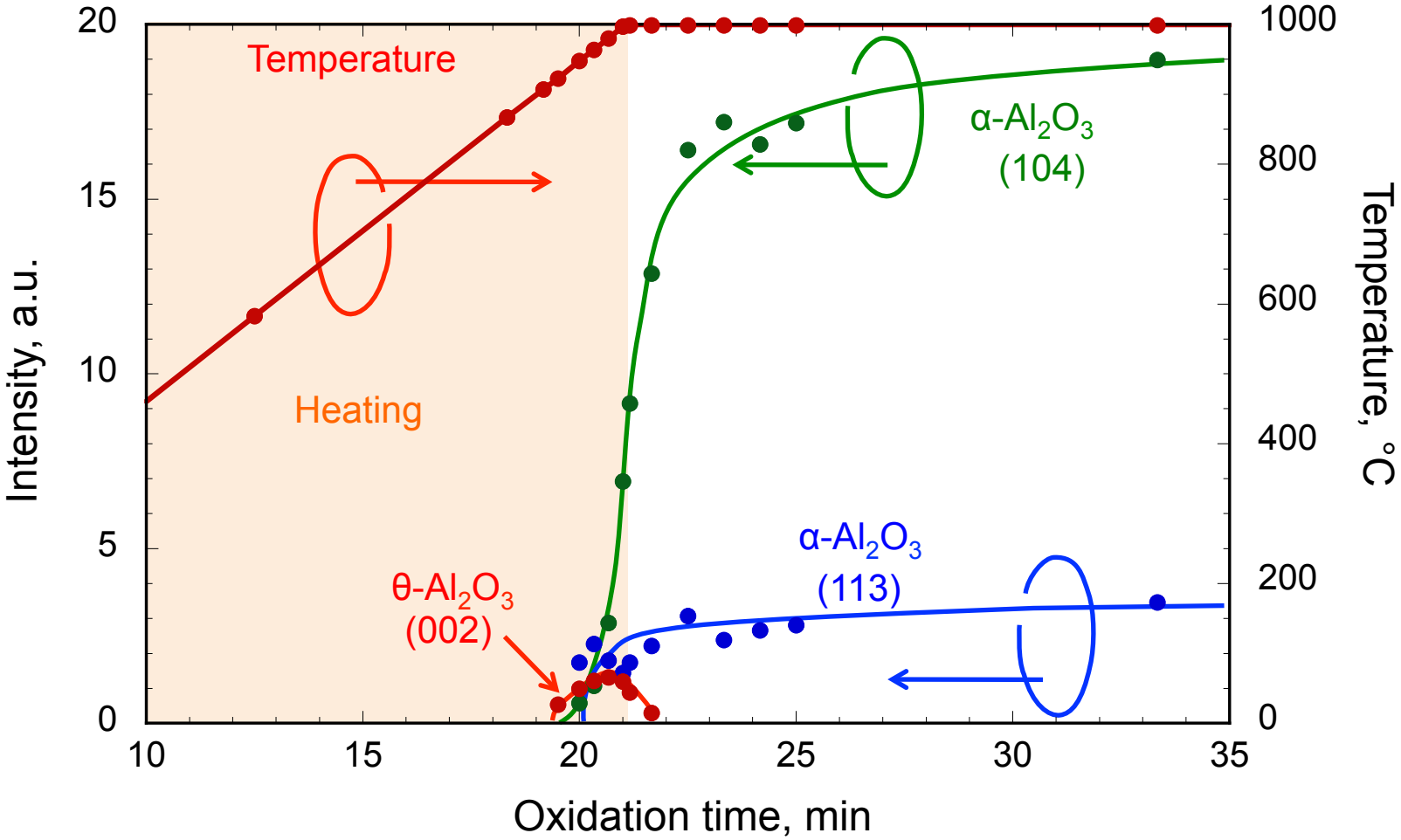
Oxidation time: 1 or 4h

Evolution of Oxide Scale during the HT Oxidation

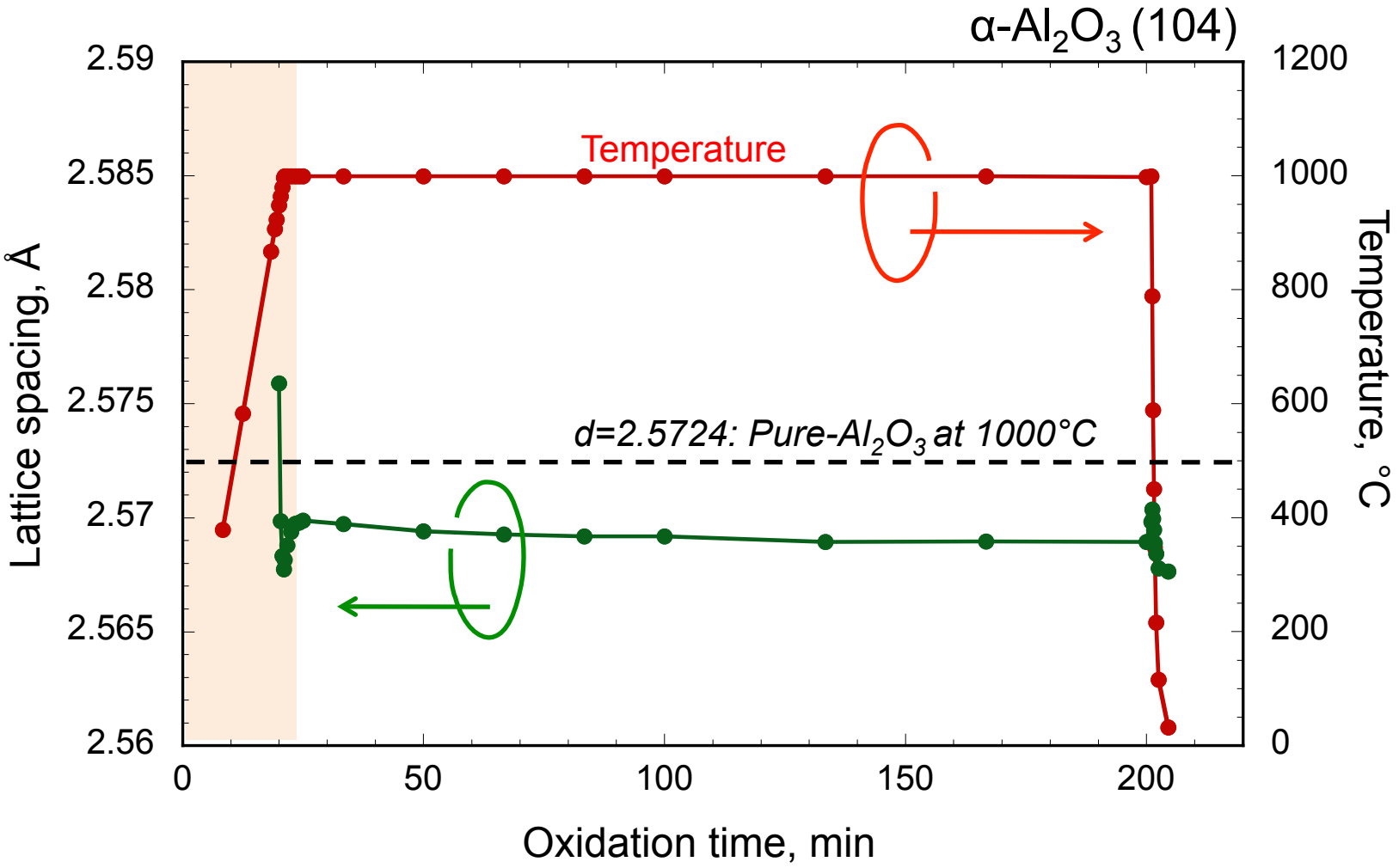
Non-coated Fe-Al at 1000°C for 4h



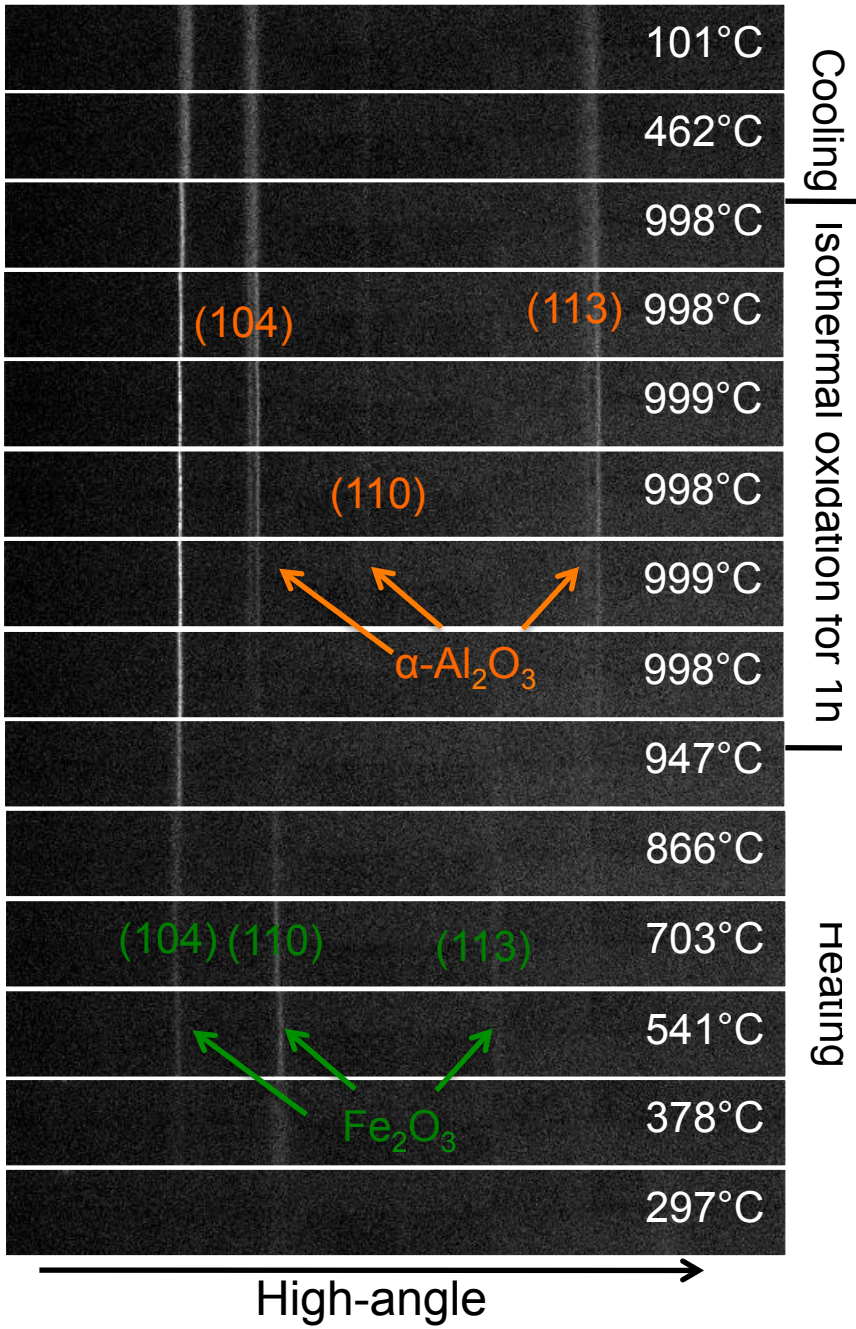
Change in Intensities of Different Al_2O_3 Phases



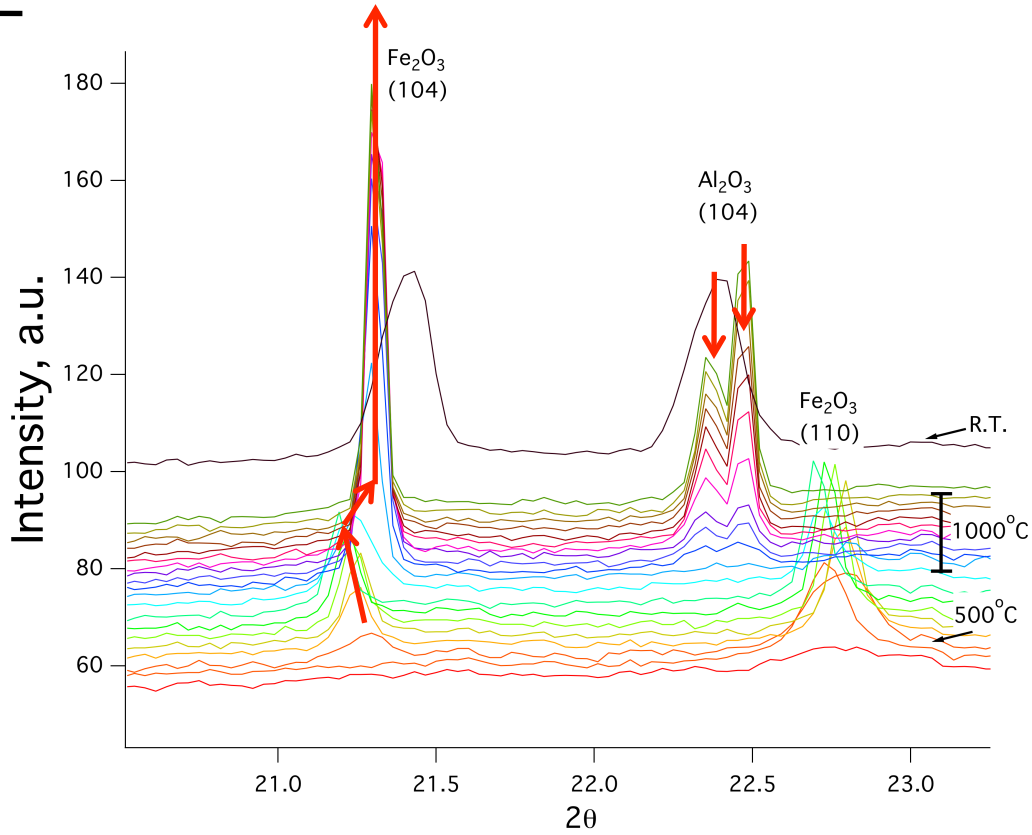
Change in Lattice Spacing of α-Al_2O_3



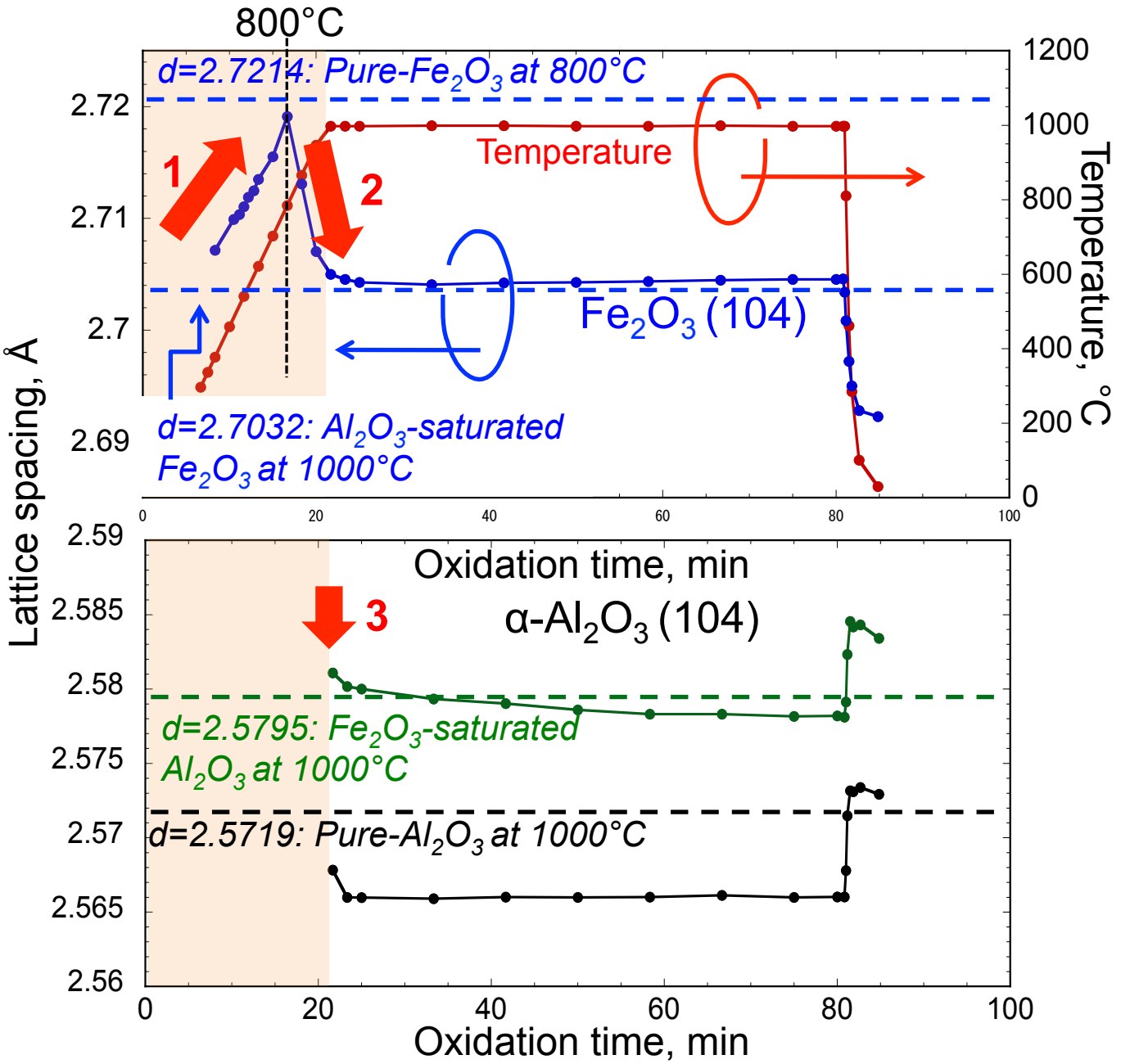
Evolution of Oxide Scale During the HT Oxidation

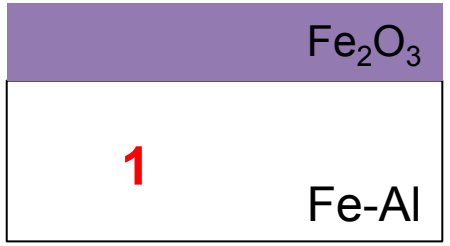


Fe-coated Fe-Al at 1000°C for 1h

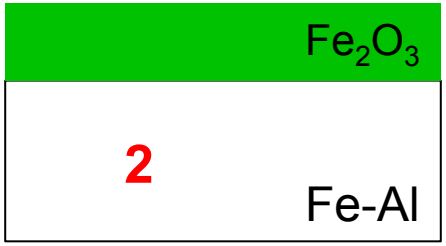


Change in Lattice Spacing of Oxide Scale

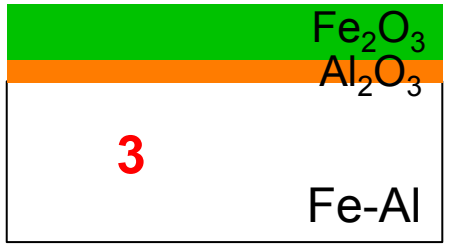




Therm. Exp. of Fe_2O_3



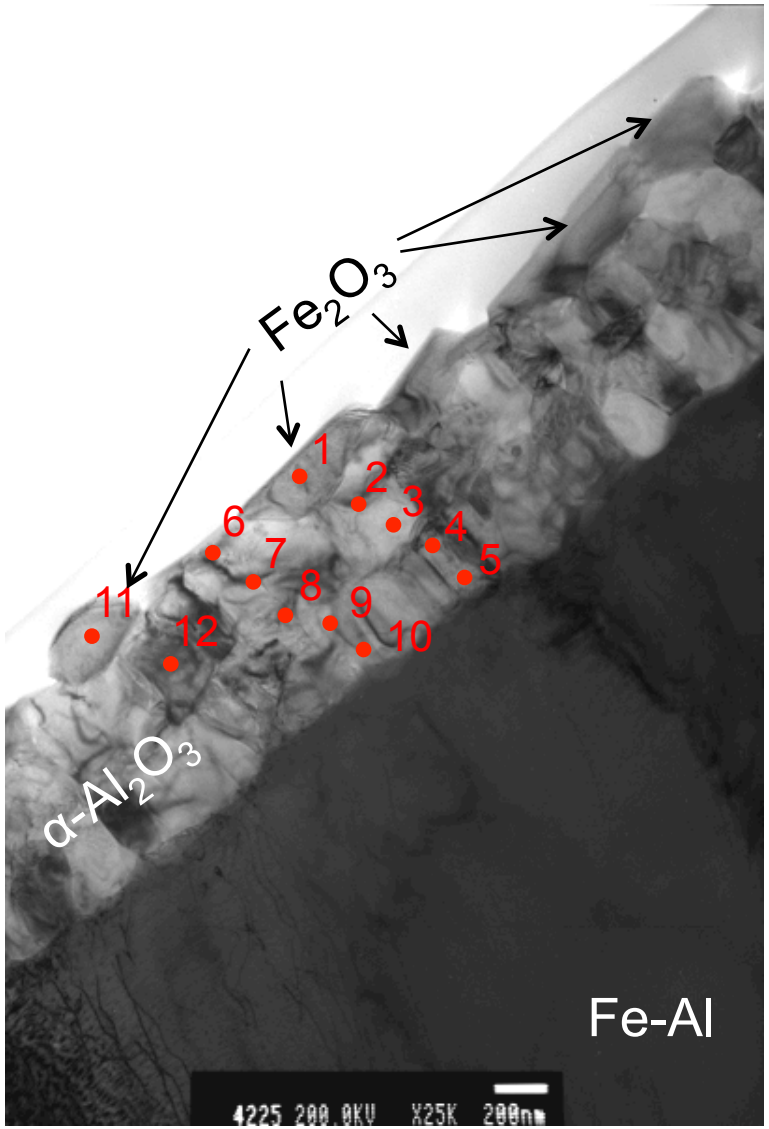
Saturation of Al_2O_3 in Fe_2O_3



Precipitation of Al_2O_3

TEM Cross-section and EDS Analysis of α-Al_2O_3

Fe-coated Fe-Al at 1000°C for 1h

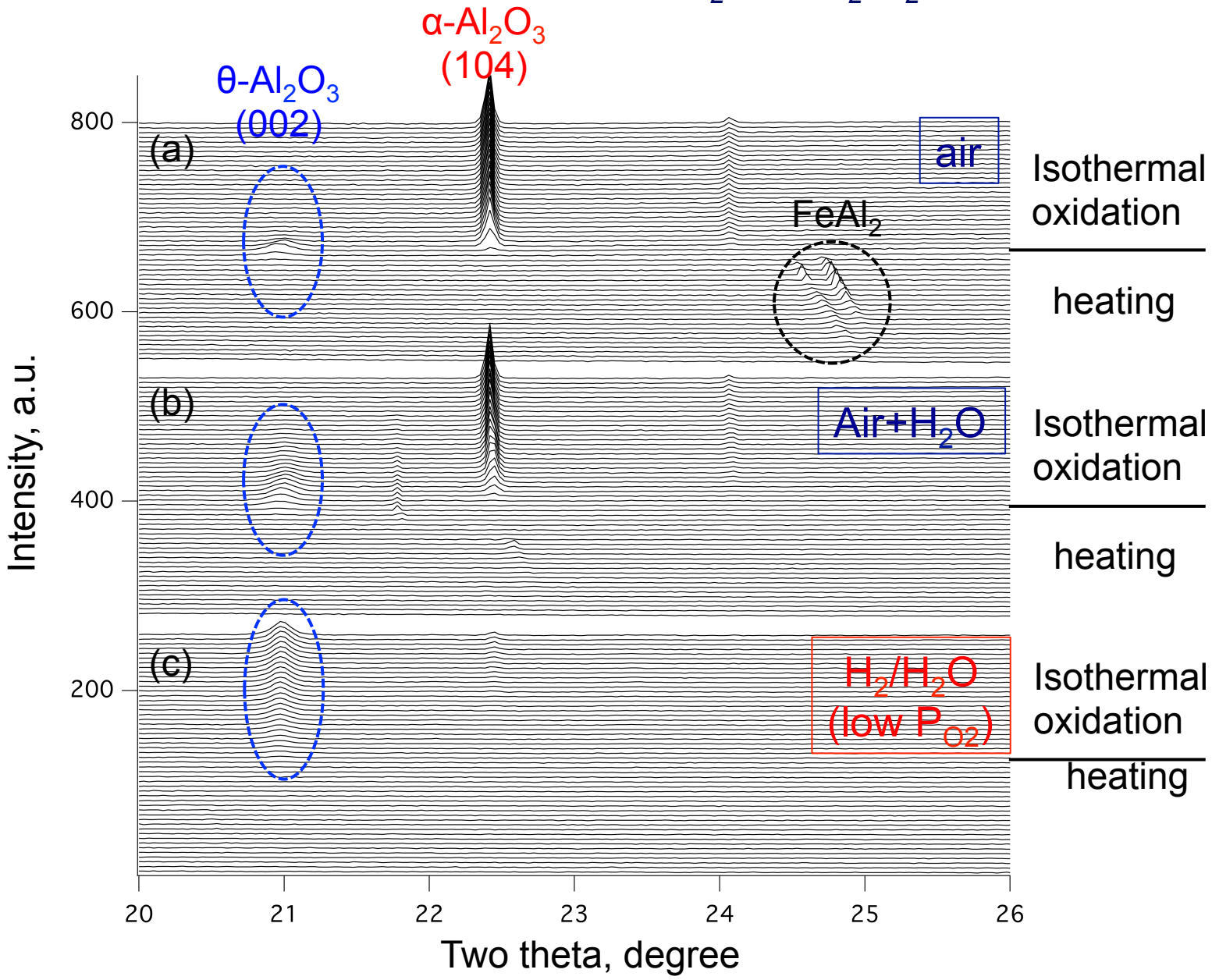


(in at.%)

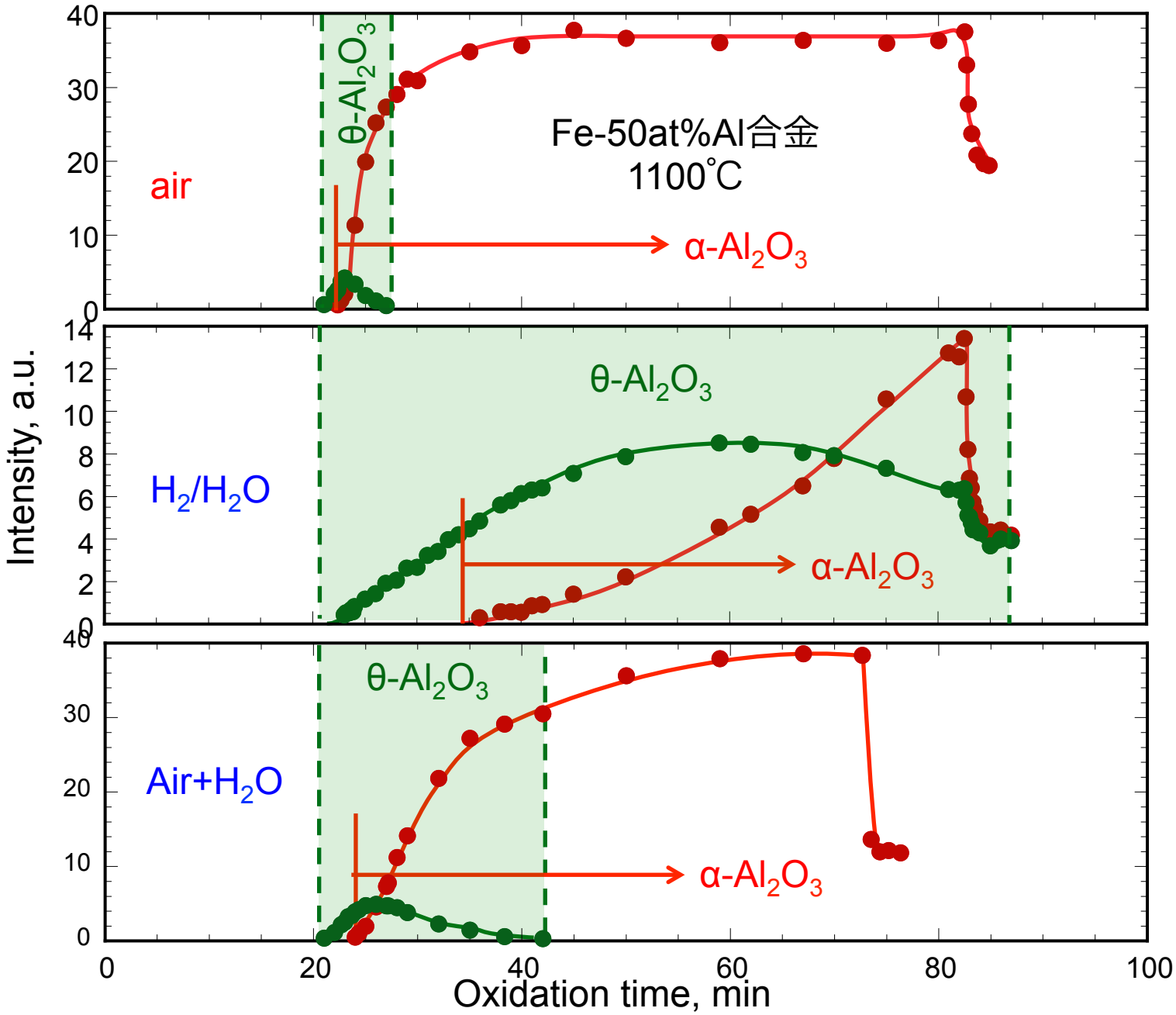
	Fe	Al	O	Solid Solution
1	42.0	7.1	50.9	14.5 mol%Al_2O_3
2	2.5	29.1	68.3	7.9 mol%Fe_2O_3
3	1.4	31.3	67.3	4.3 mol%Fe_2O_3
4	0.1	30.6	69.3	0.3 mol%Fe_2O_3
5	0.2	31.3	68.5	0.6 mol%Fe_2O_3
6	2.5	30.7	66.8	7.5 mol%Fe_2O_3
7	1.9	28.1	70.1	6.3 mol%Fe_2O_3
8	0.3	32.6	67.1	0.9 mol%Fe_2O_3
9	0.0	31.5	58.5	0 mol%Fe_2O_3
10	0.2	32.9	67.0	0.6 mol%Fe_2O_3
11	35.1	6.5	58.4	15.6 mol%Al_2O_3
12	1.2	33.9	64.9	3.4 mol%Fe_2O_3

Effect of P_{O_2} on the Transformation of Al_2O_3

Bulk Fe-52Al oxidized in air, air+H_2O or H_2/H_2O at 1100°C



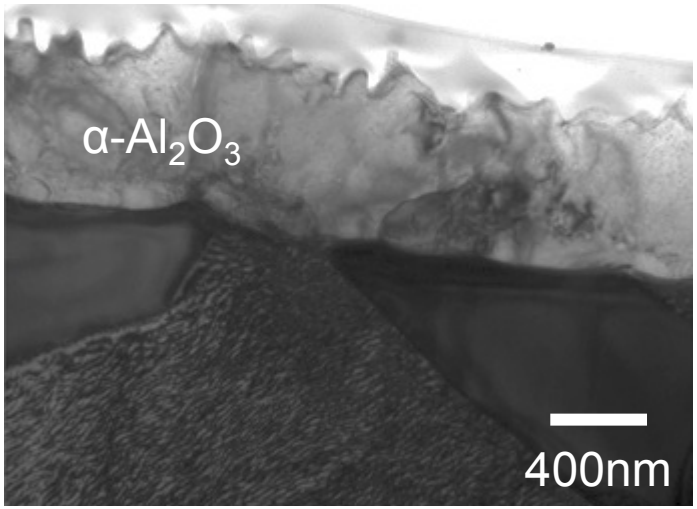
Effect of H_2O and/or P_{O2} on the Transformation to α-Al_2O_3



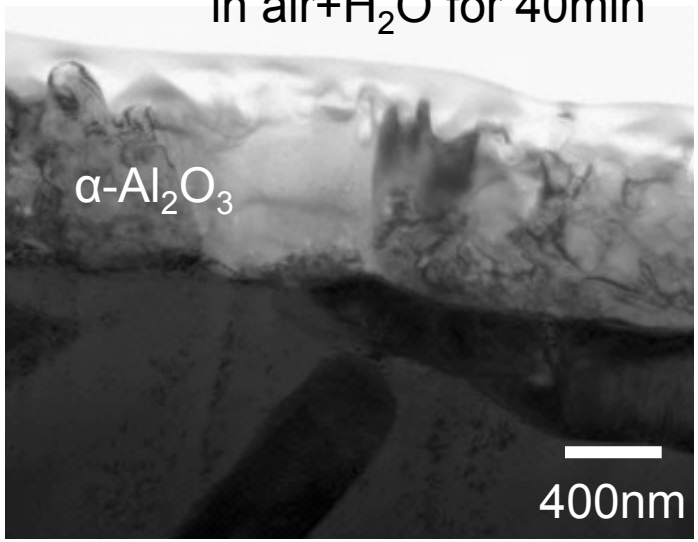
TEM Cross-sections of α-Al_2O_3

Bulk Fe-52Al at 1100°C for 1h (40min)

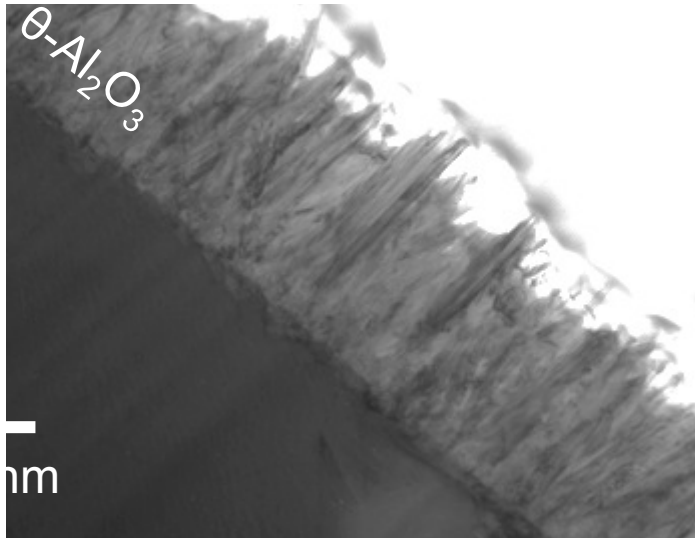
in air for 1h



in air+H_2O for 40min

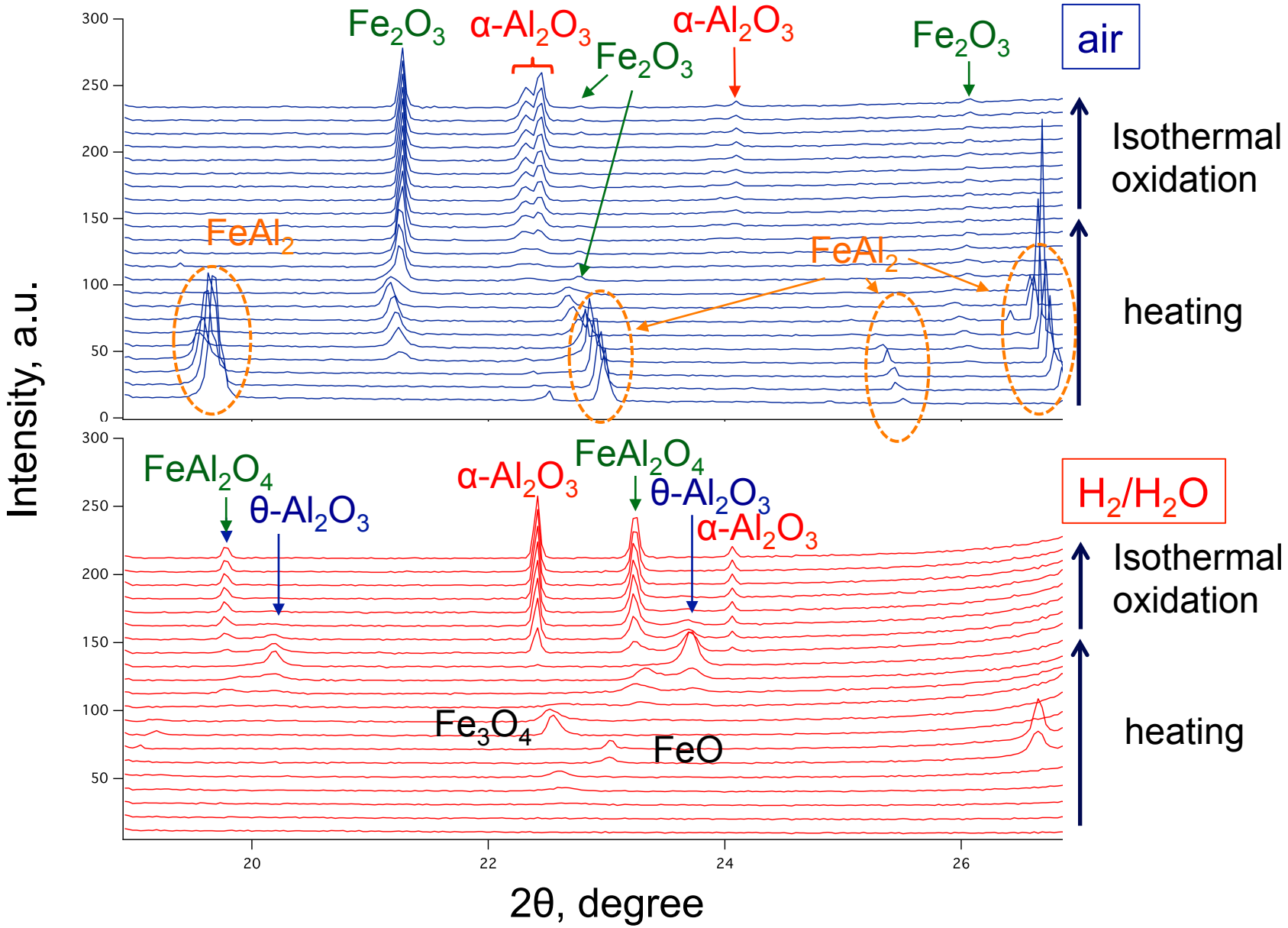


in H_2/H_2O for 1h



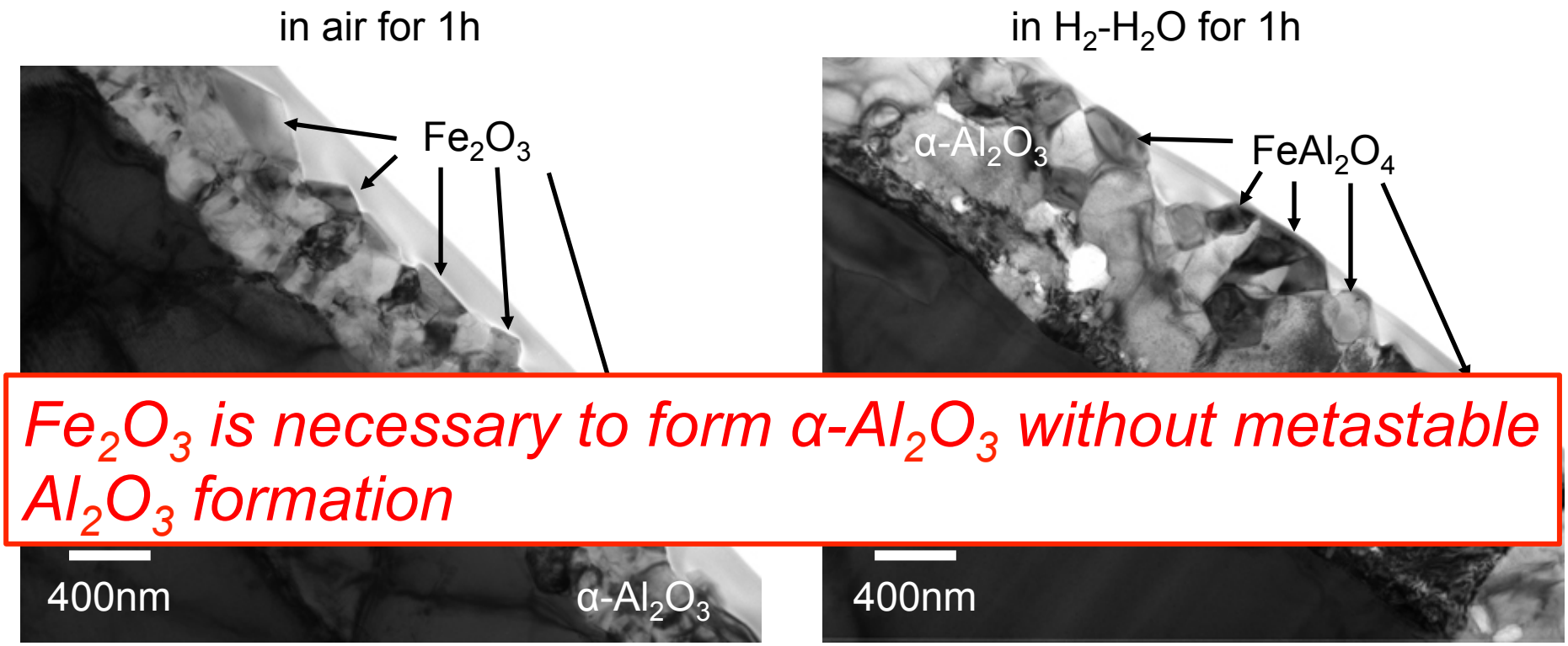
Effect of P_{O_2} on the Transformation of Al_2O_3

Fe-coated Fe-52Al oxidized in air or H_2/H_2O at 1100°C



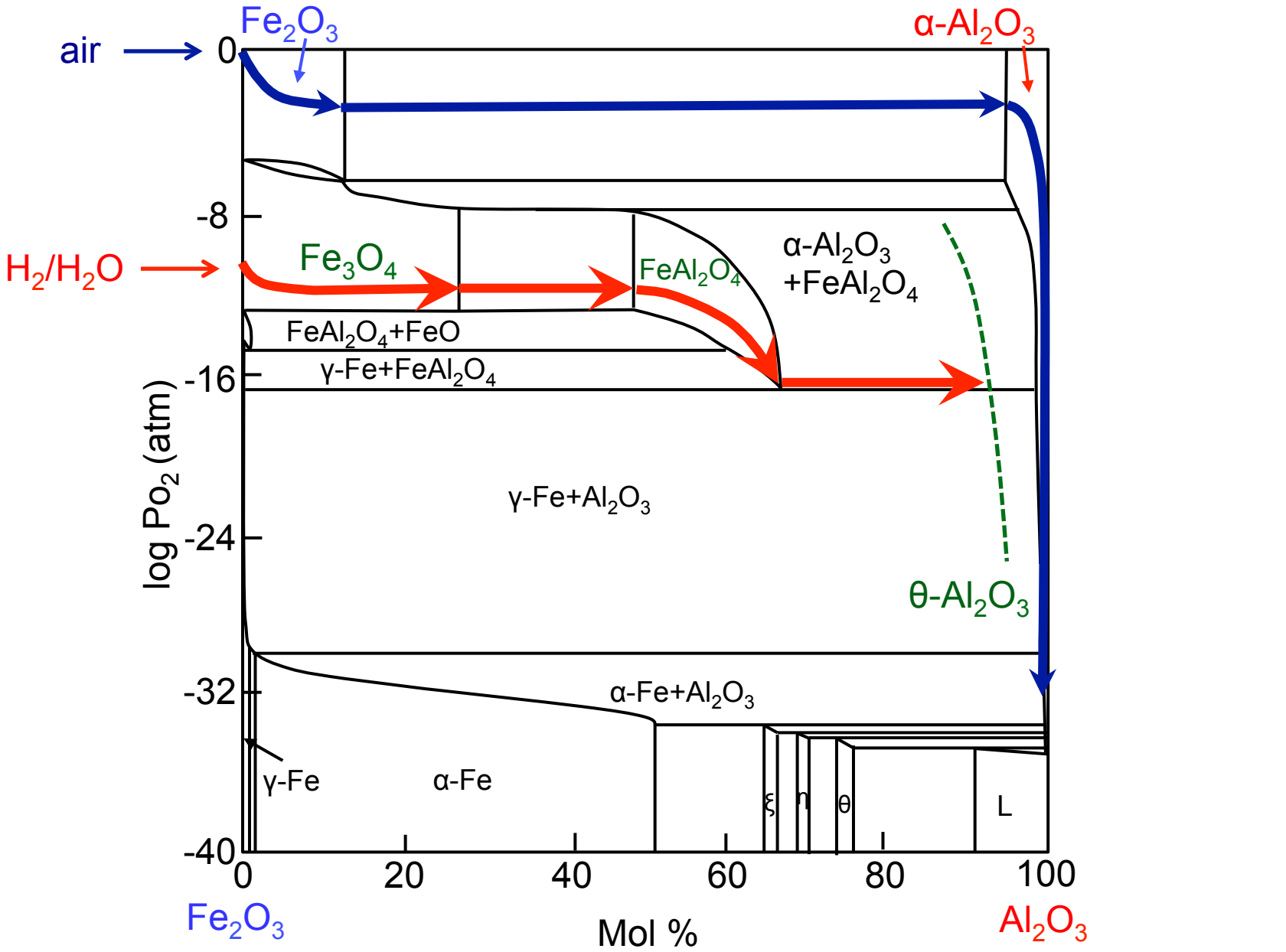
TEM Cross-sections of α-Al_2O_3

Fe-coated Fe-52Al at 1100°C for 1h (40min)



Fe_2O_3 is necessary to form α-Al_2O_3 without metastable Al_2O_3 formation

Modified Ternary Fe-Al-O System



F.A. Elrefair and W.W. Smeltzer, Met. Trans. B, (1983)

Summary

Formation of α-A_2O_3 from Fe_2O_3 was confirmed by in-situ measurement via synchrotron radiation.

Precipitation of α-Al_2O_3 (sympathetic nucleation) occurred when Fe-coated alloy was oxidized in air.

In low P_{O_2}, Metastable Al_2O_3 formed and it's transformation to α-Al_2O_3 delayed.

Transformation to α-A_2O_3 was delayed and/or metastable θ-Al_2O_3 was stabilized:

- On the alloys with lower Fe content.
- In the atmosphere with lower partial pressure of oxygen.

Lower Fe content in the metastable Al_2O_3 delayed the transformation.