Corrosion Tests of FeCr- and FeCrAl alloys in static and flowing LBE

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  - Oxidation of Metal
- Experimental
  - Test materials
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- Results and Analysis
  - Ferritic/Martensitic steels
  - Austenitic and FeCrAl steels
- Summary and future work

Introduction

- Nuclear Spent Fuel in Korea – a serious issue

Protest against Government Proposal for Spent Nuclear Fuel Interim Storage + LLW (2003)

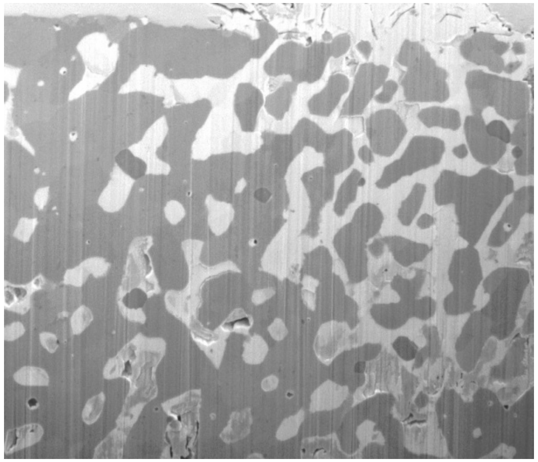
Korean Public has Welcomed Low-Intermediate Level Waste (2005)

- Fuel Cladding
  - PEACER : HT-9 at 450^{o}C for 3~5 year
  - PASCAR : at 450^{o}C for 20 year

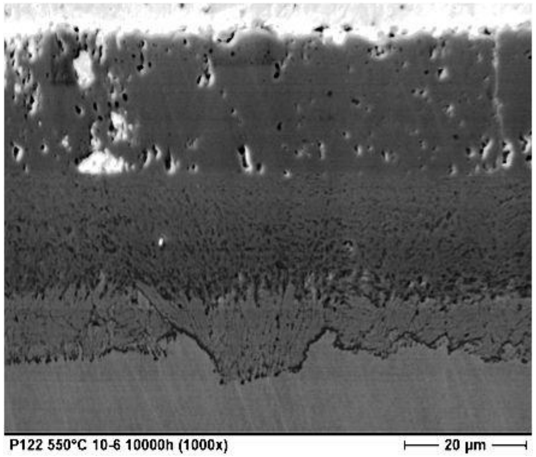
- Develop better materials for LBE

Introduction

- Because of the severe dissolution or fast oxide growth at high temperature (>500°C) in case of conventional FeCr- alloys (SS316L, HT9, T91..) in LBE, better materials are needed.



Dissolution attack

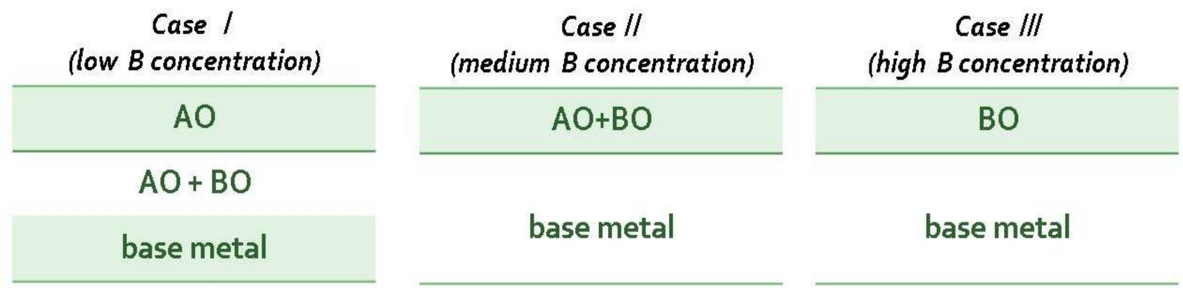


Oxidation damage

- For high temperature (>500°C) applications, Al-containing alloy and Al-coated steels (GESA treatment by FZK) have shown promise in addition to Russian Si-containing alloys.

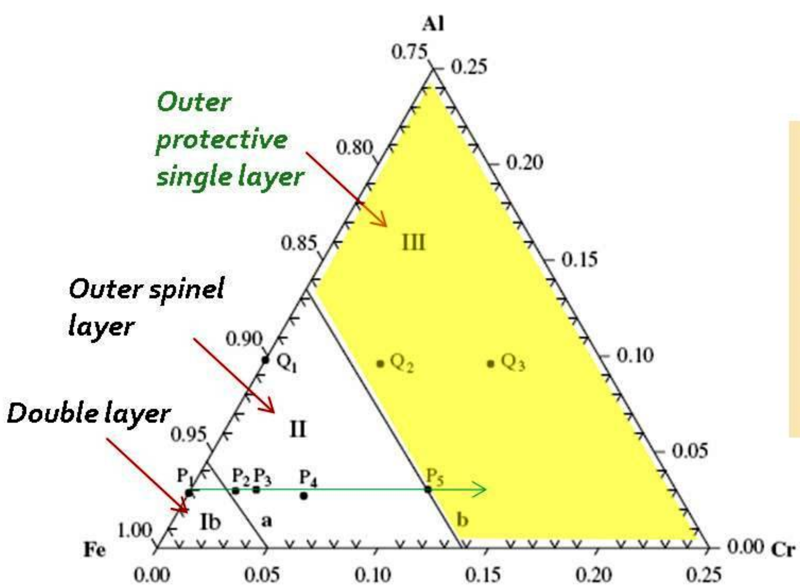
Literature Review - Oxidation of Fe-Cr-Al Alloys

- Fe-Al binary alloy
  - The development of external Al_2O_3 on binary Fe-Al alloys requires critical Al levels (above 13%) generally leading to unacceptable mechanical properties.



Schematic models of the general scale growth on A-B alloys

- Cr addition in Fe-Al alloy (Third Element Effect)



The addition of B to an A-C alloy can reduce the critical concentration to establish an external scale of the C oxide : A is the most noble and C is the most reactive component, while B has an oxygen affinity intermediate between those of A and C.

Literature Review - Oxidation of FeCrAl alloys

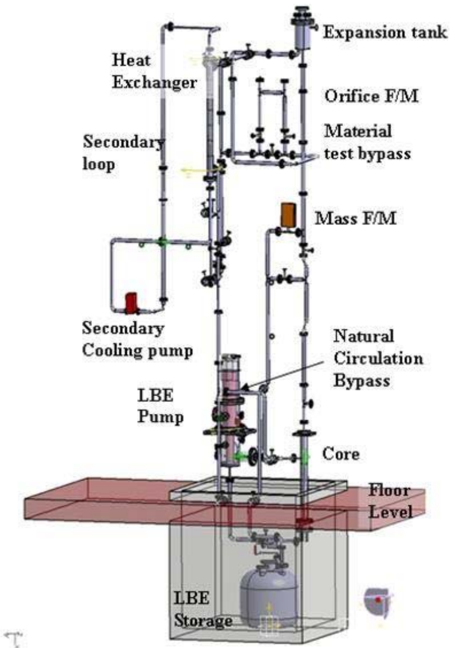
- Sulfur segregation at thermally grown Al_2O_3/alloy interface
  - During high temperature oxidation of alumina forming alloys, Sulfur consistently segregate at the growing interface; Its presence weakens the interfacial bonding of oxide.
  - Where Cr is present, the amount of S at the interface is much higher.
  - The segregation of sulfur tends to vary with time and temperature owing to the dynamic nature of the oxidation process.

- Reactive Element Effect
  - REE is effect of the elements have high negative free energies of oxide formation.
    (ex) Yttrium, Cerium, lanthanum, Hafnium
  - The presence of small amount of reactive elements in the alloy :
    - reduce the S activity in the alloy, preventing S segregation to interface.
    - greatly improve Al_2O_3 scale adhesion
    - Reduce oxide growth rate

Experimental – Test Materials

Material	Fe	Cr	Ni	Al	Si	Mn	Mo	Y_2O_3	Ti	Y	Zr	
SS316L	Bal.	17.3	12.1		0.35	1.8	2.31					*ASS*
HT9	Bal.	11.5	0.5		0.3	0.6						*FMS*
T91	Bal.	8.6	0.23		0.3	0.43	0.95					*FMS*
EP823	Bal.	12	0.8		1.3	0.8	0.9					*FMS*
PM2000	Bal.	20		5.5				0.5	0.5	-	-	*OD*
MA956	Bal.	20		4.8				0.5	0.4	-	-	*OD*
KANTHAL-AF	Bal.	22		5.3	0.21	0.17		-	0.07	0.03	0.05	FeCrAlY

Experimental – Apparatus

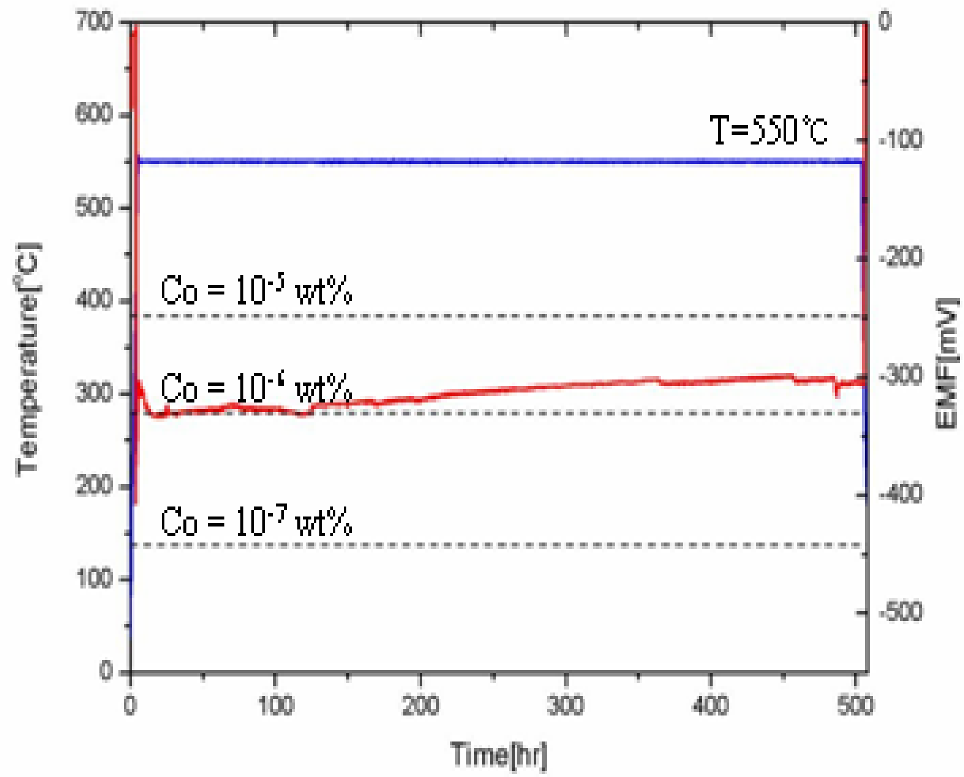


HELIOS : non-isothermal, flowing LBE Test

Static cells (left) and oxygen control system (right)

Experimental –Corrosion Test Conditions

Specimen	
Specimen type (size)	Sheet (25x 8x1 mm)
Surface treatment	Polished by SiC paper up to 600grit
Static Test condition	
LBE quantity	9kg
Test Temperature	450°C, 500℃, 550℃
Oxygen in LBE	10^{-6} ~ 10^{-5} wt%
Oxygen control	Mixture of H_2/H_2O gas
Dynamic Test condition	
LBE quantity	1700kg
Test Temp, velocity	450°C, ~2m/sec
ΔT, oxygen in LBE	200°C, 10^{-6} ~ 10^{-5} wt%
Method s of analysis	
FIB-FESEM, STEM, EDS, EPMA	



Measured Temperature and Oxygen Potential in the Test Section

- YSZ (Bi/Bi2O3)
- Red line : Oxygen potential (EMF)

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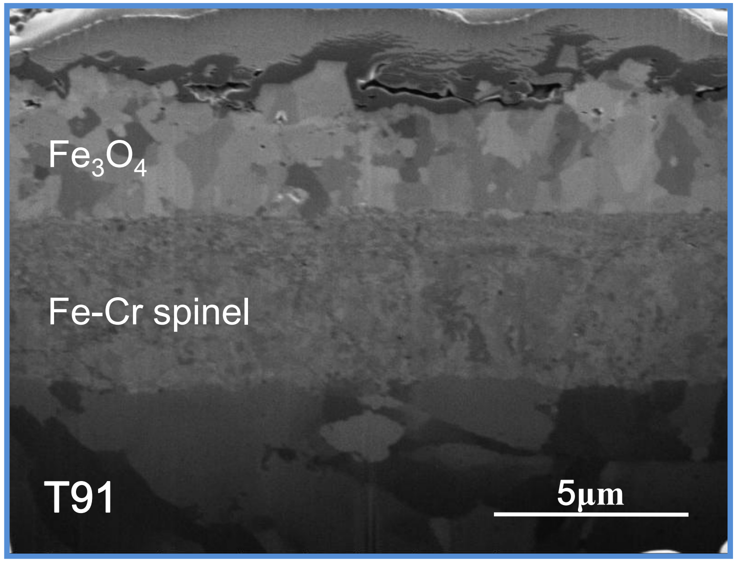
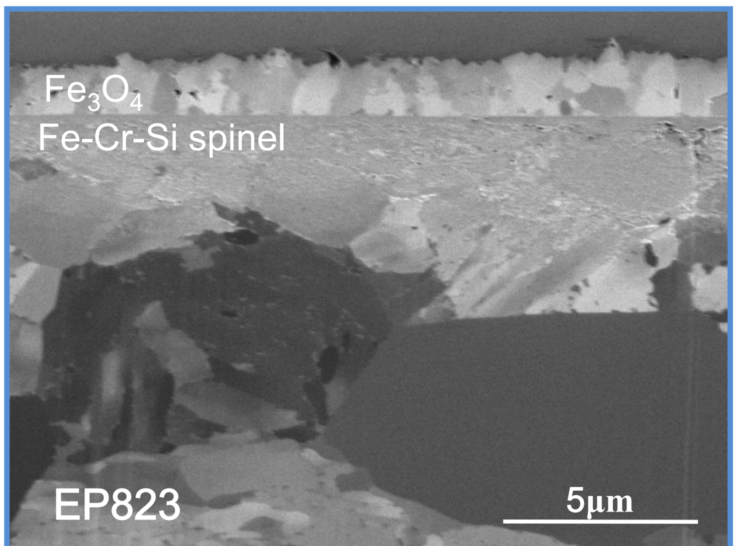
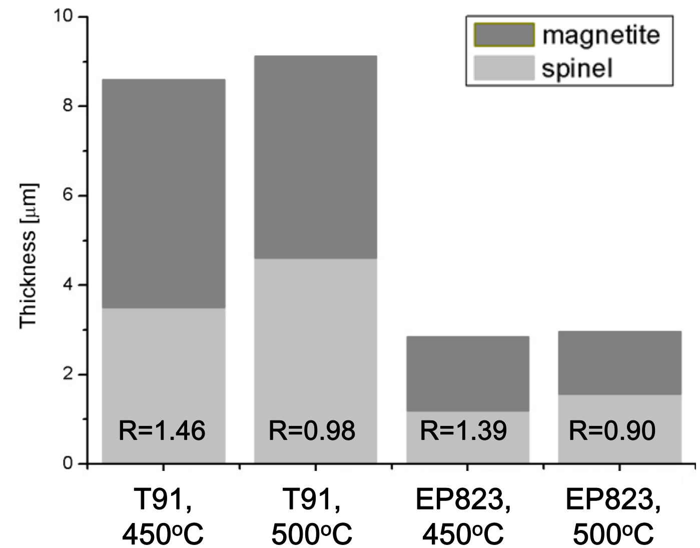
Results – Ferritic/martensitic SS



Cross section : 500°C, 500hr, static LBE



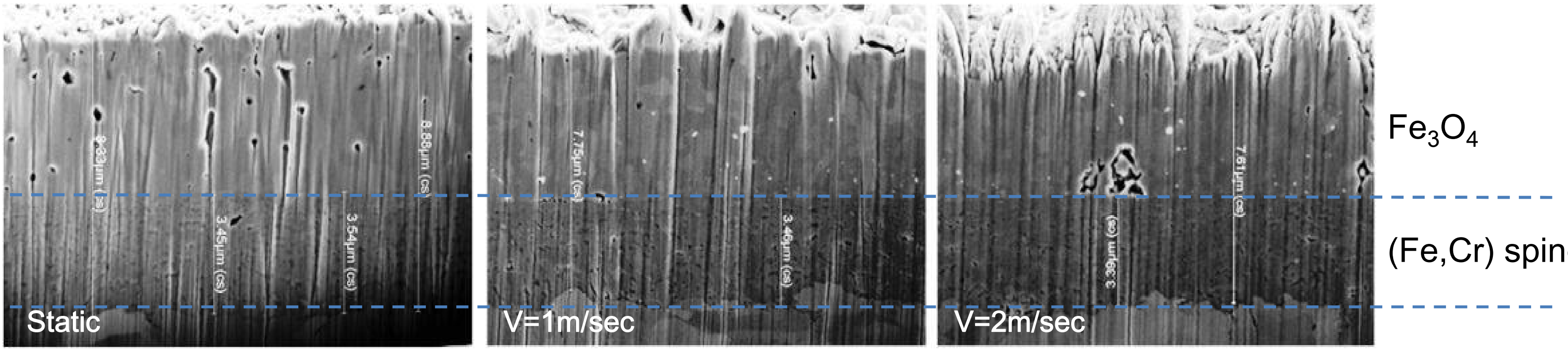


Temperature effect in static LBE

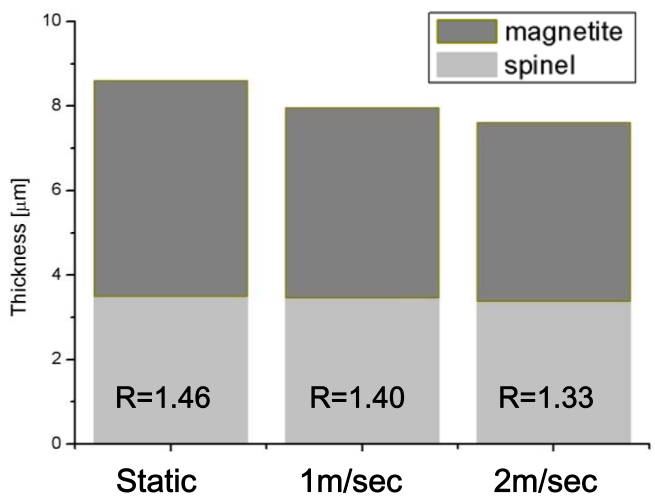
*R= thickness of magnetite/thickness of spinel

- The magnetite to spinel thickness ratio is reduced as temperature increases.
- The ratio should depends on Fe dissolution and spallation of magnetite in static LBE

Results – Ferritic/martensitic SS (flow effect)



Cross sections of T91 : 450°C, 500hr, static and flowing LBE



Flow effect - T91, 450°C,500hrs

- The magnetite to spinel thickness ratio is reduced as the flow velocity increases.
- But the effect of flow velocity on the magnetite growth is smaller than that of temperature.
- The spinel layer growth rate is independent of the LBE flow rate.

*R= thickness of magnetite/thickness of spinel

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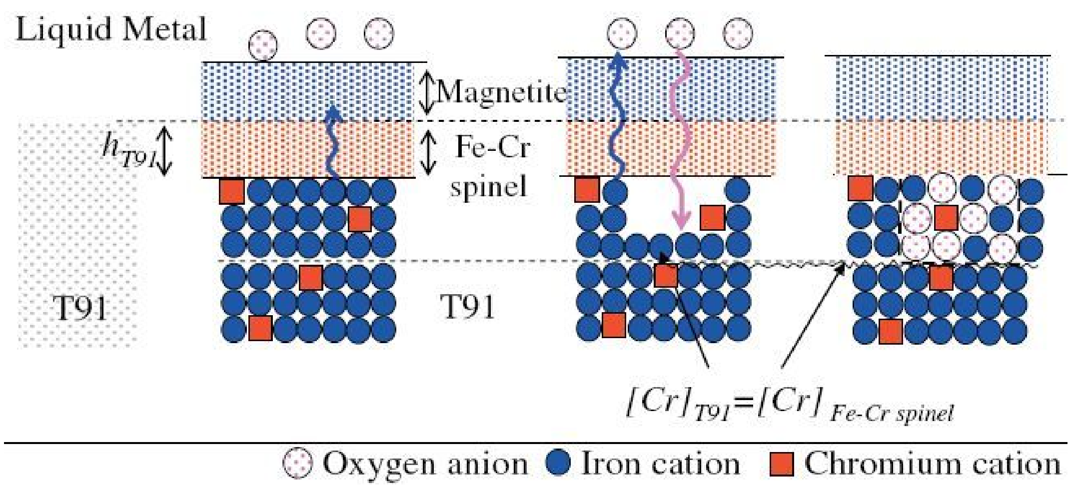
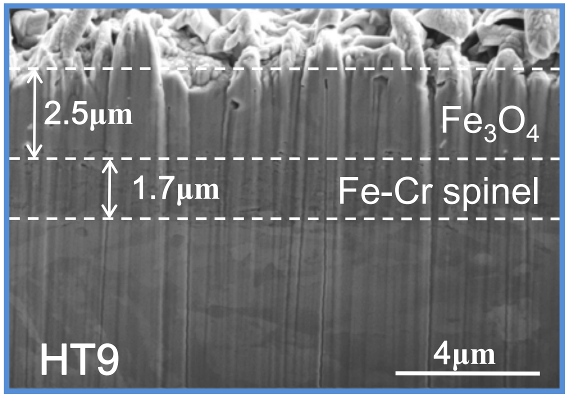
Oxidation kinetics of Ferritic/Martensitic Steels in LBE



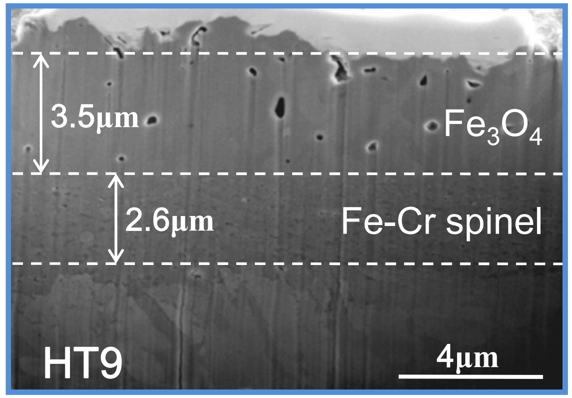
"Available space model" – the Fe-Cr spinel growth rate depends on the iron diffusion across the oxide scale
(L.Martinelli, Corrosion Science, vol 50, 2008)

- According to available space model,
  - $R = h_{mag}/h_{sp} =$ constant (if there are no dissolution, erosion, spallation of magnetite)
  - $(h_{sp})^2 = k_{sp}t$
  - $(h_{mag})^2 = k_{mag}t = R^2 k_{sp}t$
  - $h_{total} = k_{total}t = h_{sp} + h_{mag} = (1+R)h_{sp} = (1+R)(k_{sp}t)^{1/2}$

Parabolic constant of FMS steels at 450°C

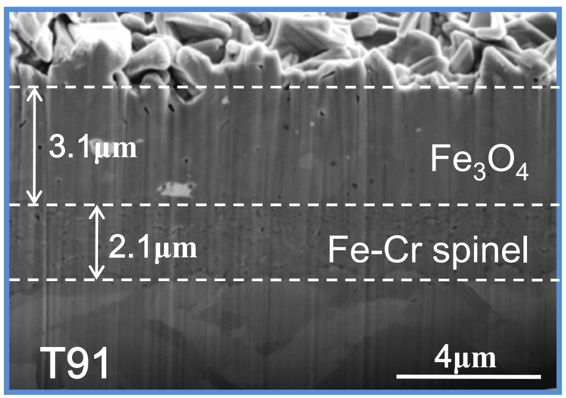


HT9, 450°C, 200hr, v=1m/sec

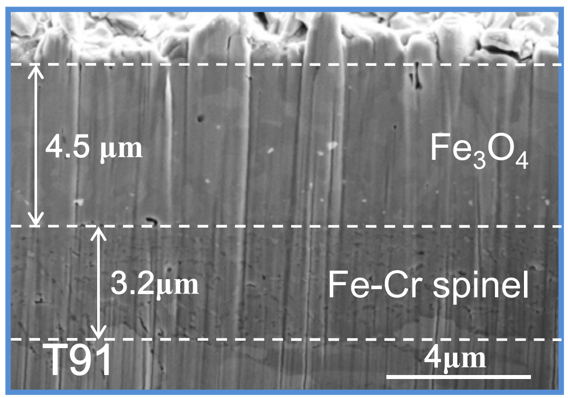


HT9, 450°C, 500hr, v=1m/sec

Parabolic constant of HT9	
k_{sp}	3.583E-14 [cm²/sec]
k_{total} (R=1.5)	2.240E-13 [cm²/sec]
k_{total} (R=1.0)	1.433E-13 [cm²/sec]



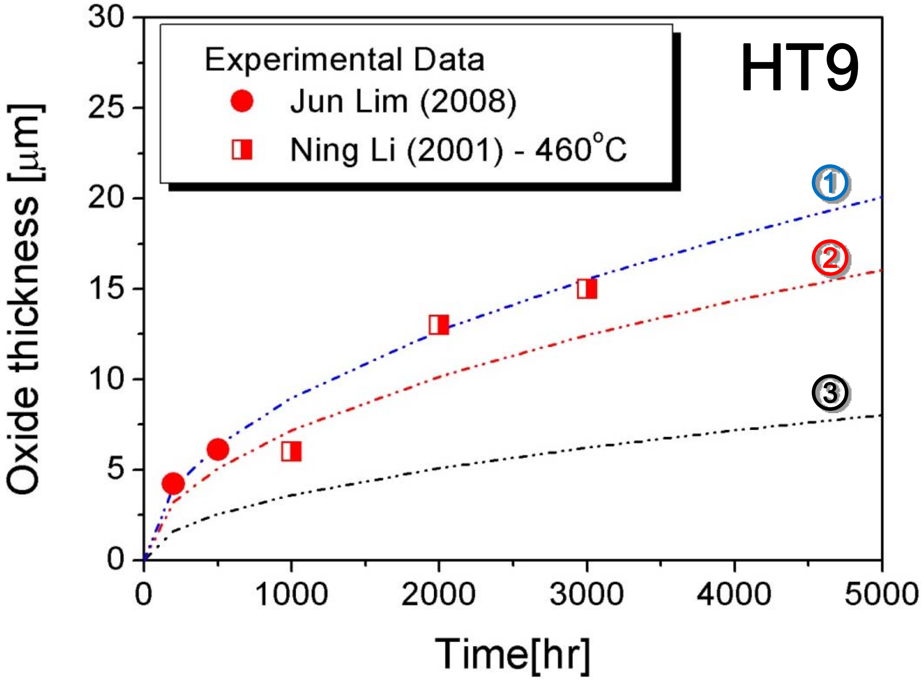
T91, 450°C, 200hr, v=1m/sec

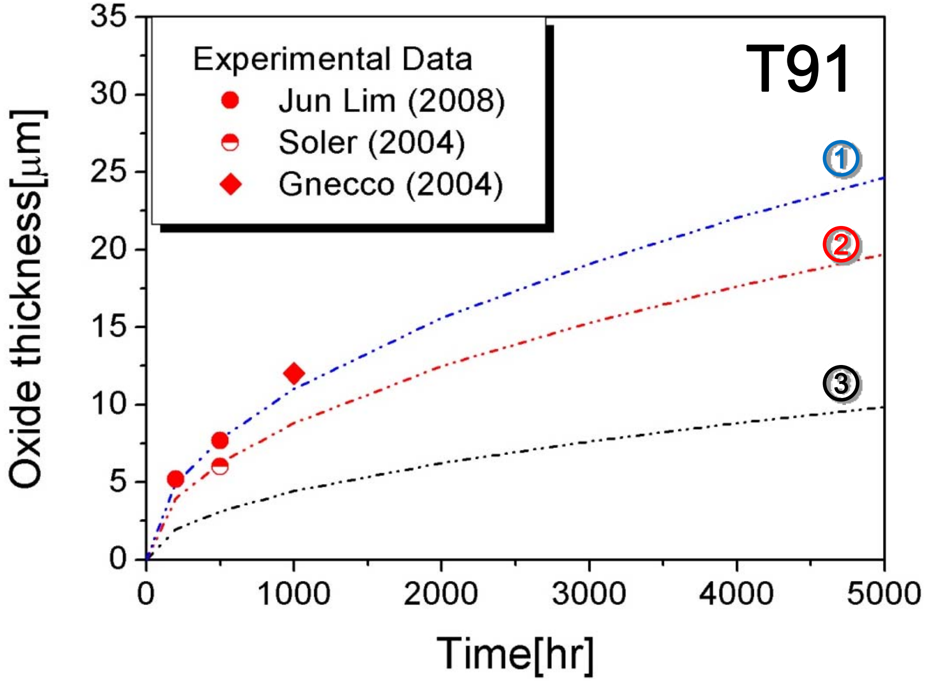


T91, 450°C, 500hr, v=1m/sec

Parabolic constant of T91	
k_{sp}	5.398E-14 [cm²/sec]
k_{total} (R=1.5)	3.374E-13 [cm²/sec]
k_{total} (R=1.0)	2.159E-13 [cm²/sec]

Oxidation kinetics of Ferritic/Martensitic Steels in LBE at 450°C



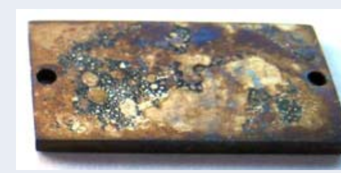
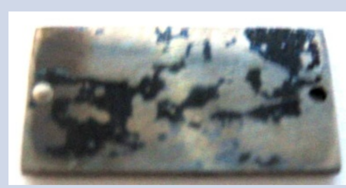


① : *calculated total oxide thickness (R=1.5)*
② : *calculated total oxide thickness(R=1)*
③ : *calculated spinel layer thickness*

Predicted oxide thickness at 450°C (R=1.5)

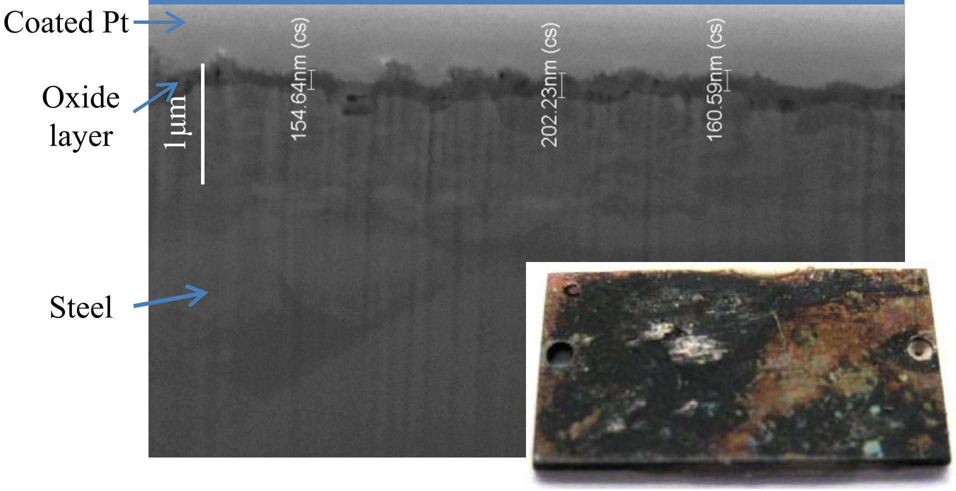
material	1 year	3 year	5 year
HT9	26.6μm	46.0μm	84.0μm
T91	32.6μm	56.5μm	103.2μm

Results – Austenite SS and FeCrAl alloys

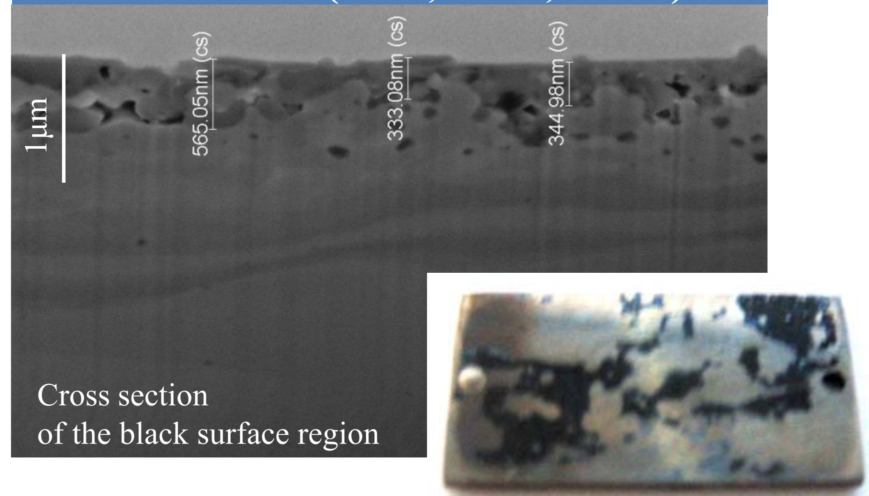
condition	SS316L	Kanthal-AF	MA956	PM2000
450^{o}C 500hrs				
450^{o}C 1000hrs				
500^{o}C 500hrs				

Results : 500°C for 500hrs

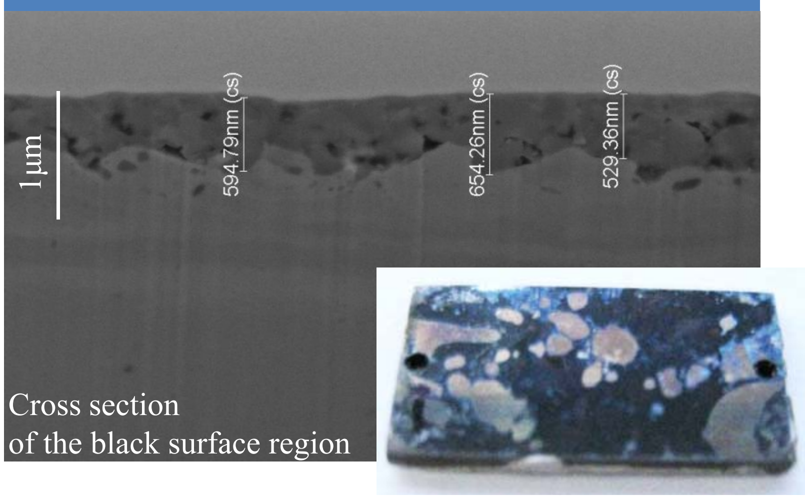
SS316L



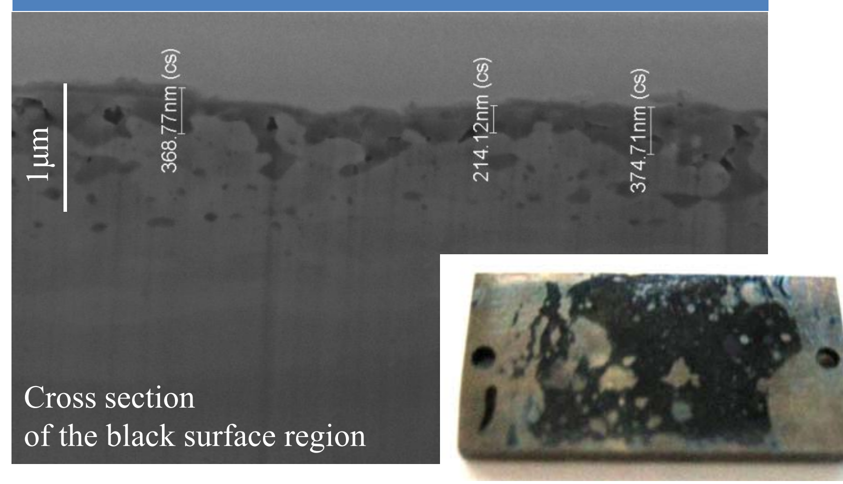
Kanthal-AF (22Cr, 5.3Al, 0.03Y)



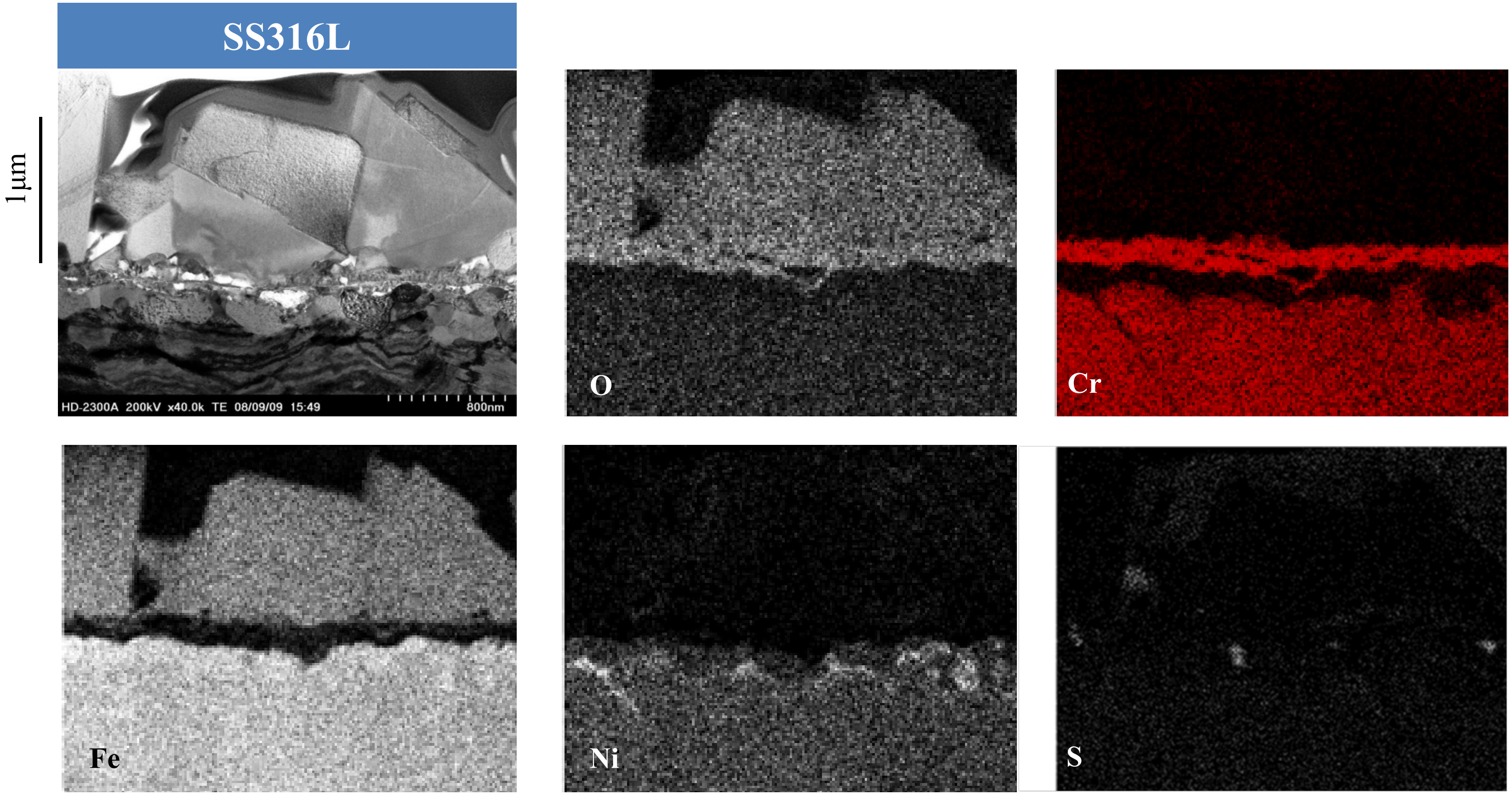
MA956 (20Cr, 4.8Al, 0.5Y_2O_3)



PM2000 (20Cr, 5.5Al, 0.5Y_2O_3)

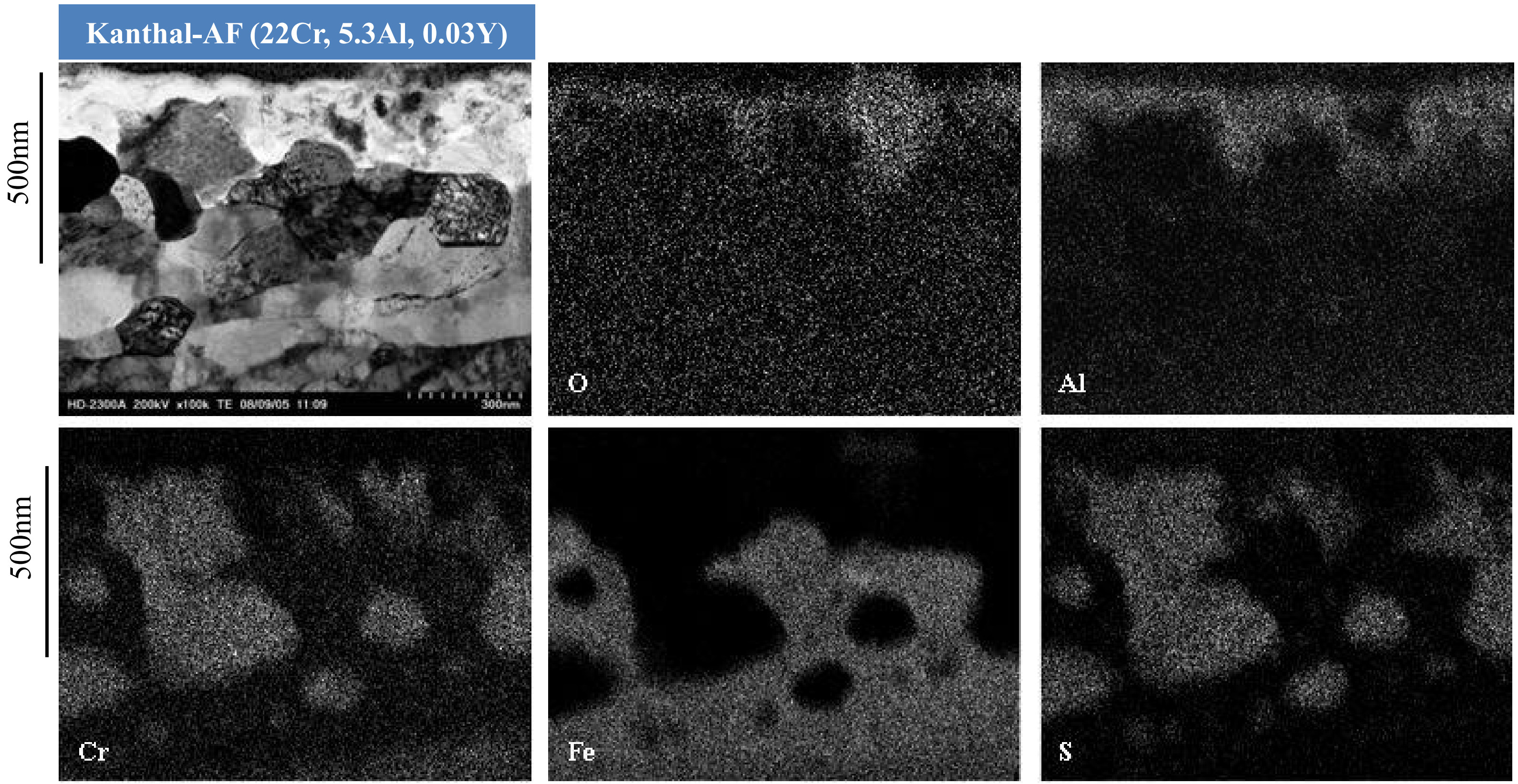


Results - STEM images and EDS analysis (500^{o}C results)



- ***Cr_2O_3** – about 200nm thick, continuous, voids*
- ***Fe_3O_4** – about 1um thick, outer growth*

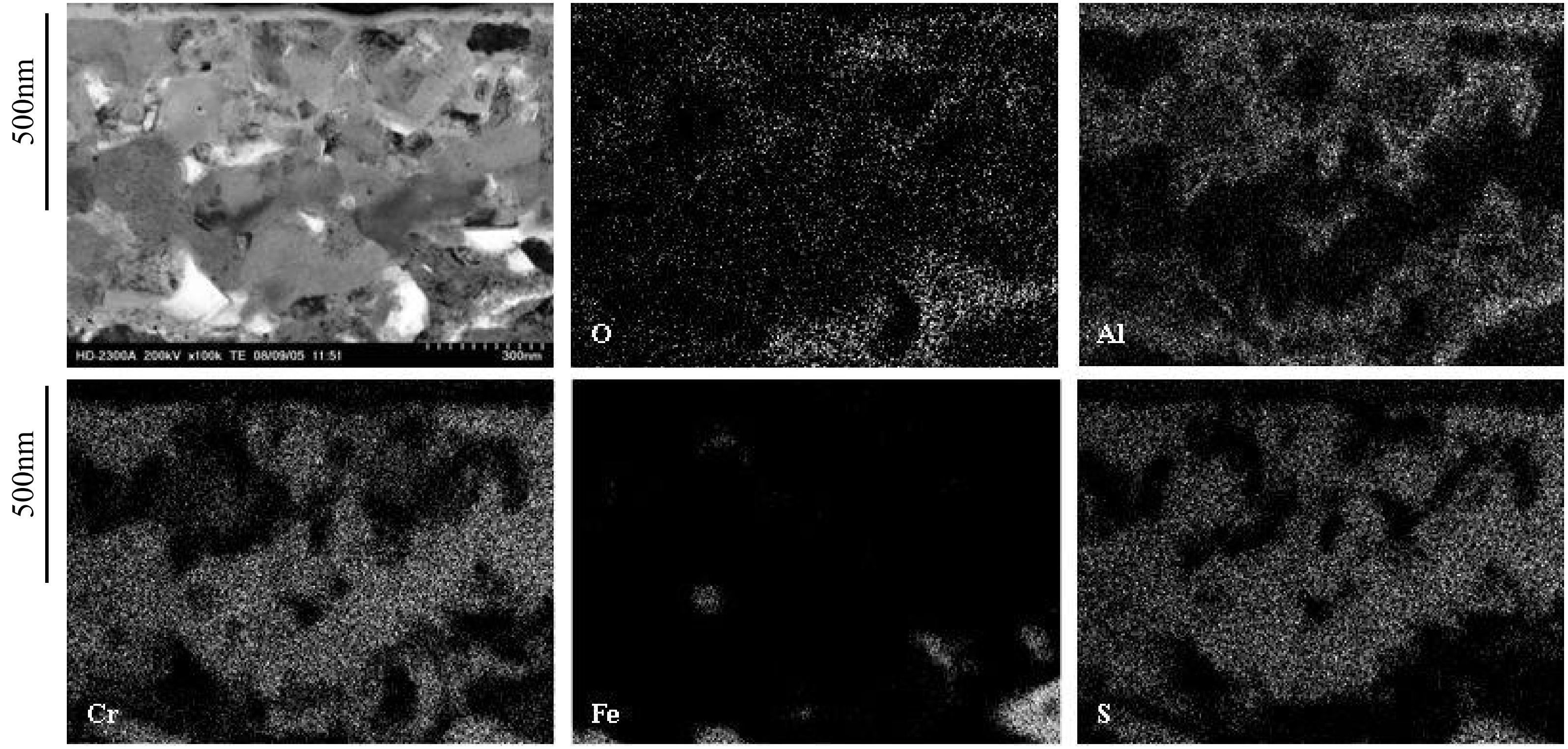
Results - STEM images and EDS analysis (500^{o}C results)



- ***Al_2O_3*** *– 50nm~200nm thick, continuous, inward growth*
- ***Cr, S enriched island*** *– about 700nm thick, at the oxide/steel interface*

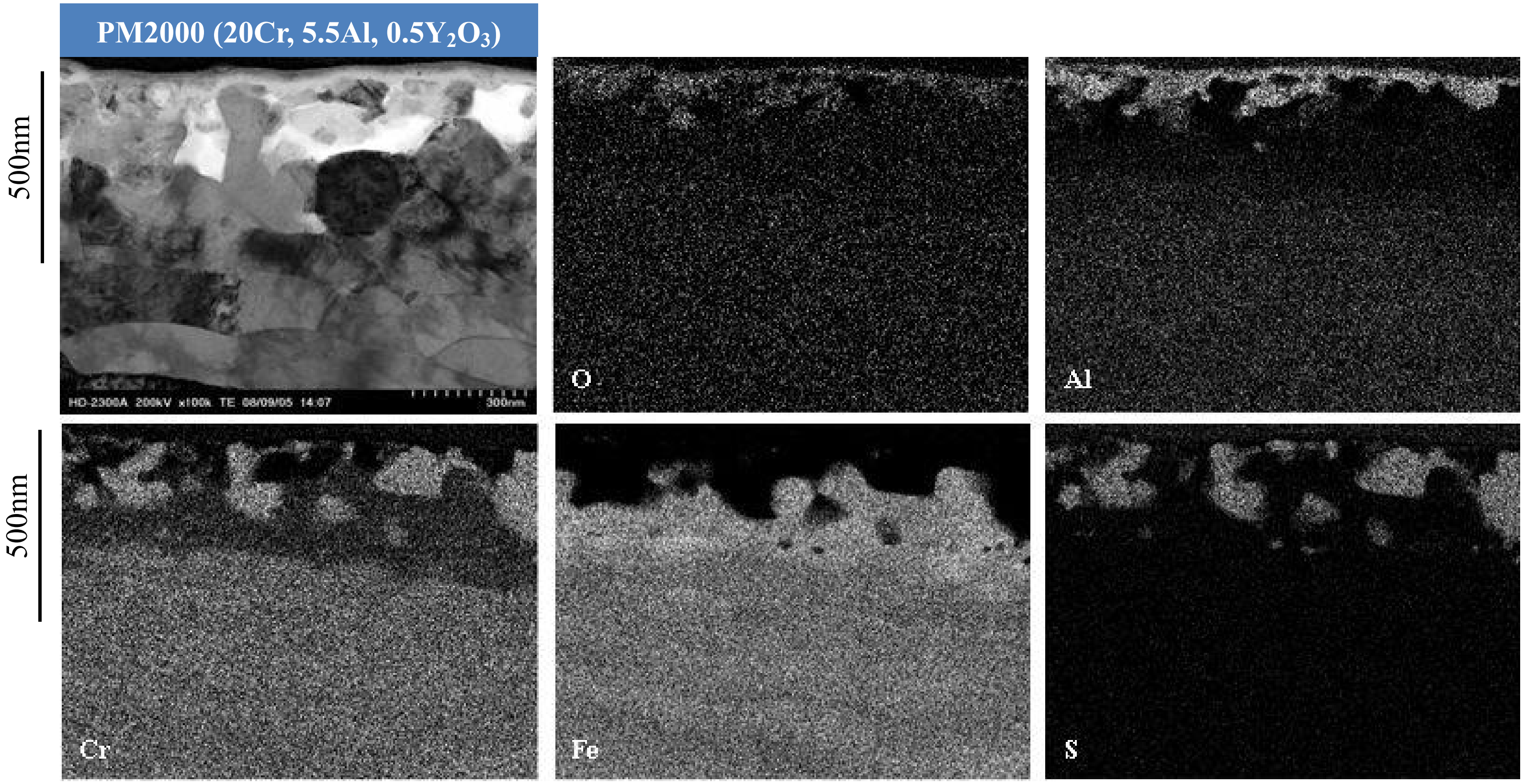
Results - STEM images and EDS analysis (500°C results)

MA956 (20Cr, 4.8Al, 0.5Y_2O_3)



- ***outer Al_2O_3*** – *50nm~500nm thick, continuous, inward growth*
- ***Cr, S enriched island*** – *500~800nm thick, at the outer/inner Al_2O_3 interface*
- ***inner Al_2O_3*** – *about 200nm thick*
- ***Voids*** – *at the oxide/sulfide interface*

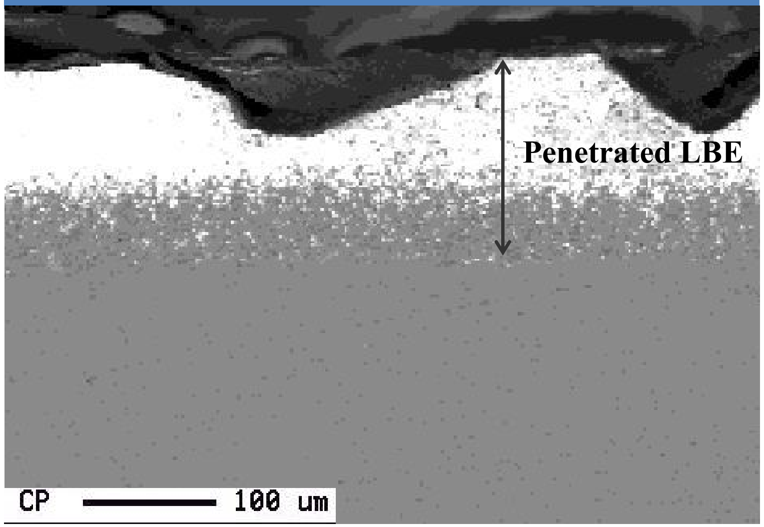
Results - STEM images and EDS analysis (500^{o}C results)



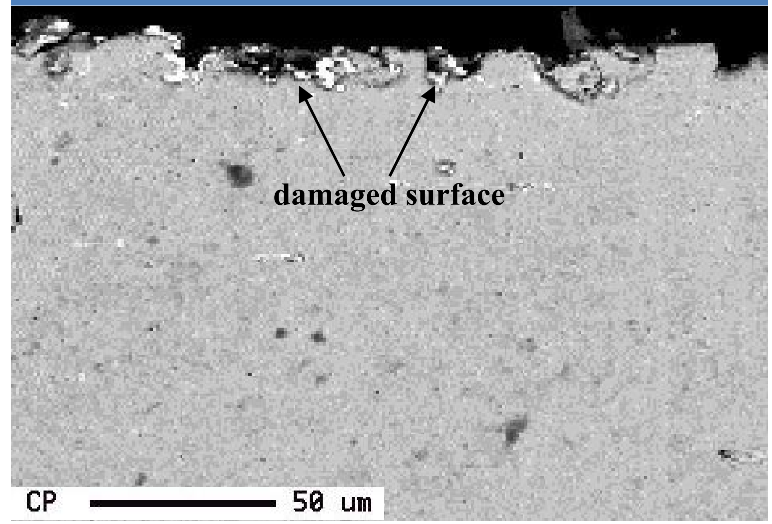
- ***Al_2O_3*** – 30nm~200nm thick, continuous, inward growth
- ***Cr, S enriched island*** – about 300nm thick, at the oxide/steel interface
- ***Voids** – at the oxide/sulfide interface*

Results : 550^{o}C for 500hrs

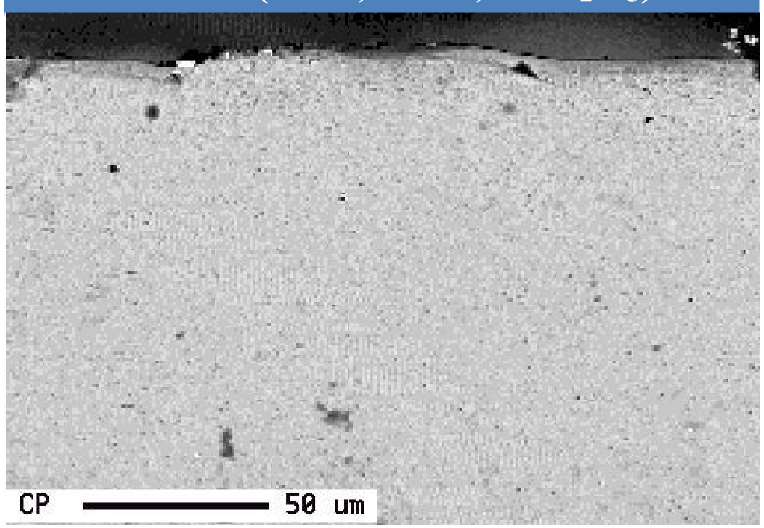
SS316L



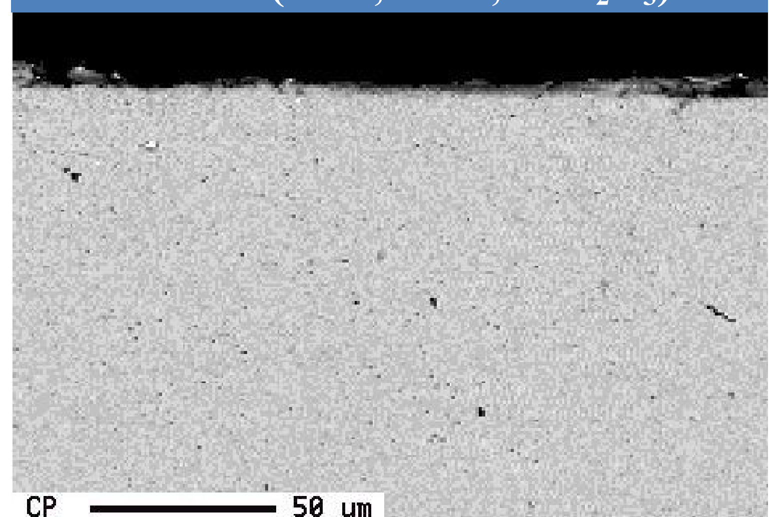
Kanthal-AF (22Cr, 5.3Al, 0.03Y)



MA956 (20Cr, 4.8Al, 0.5Y_2O_3)

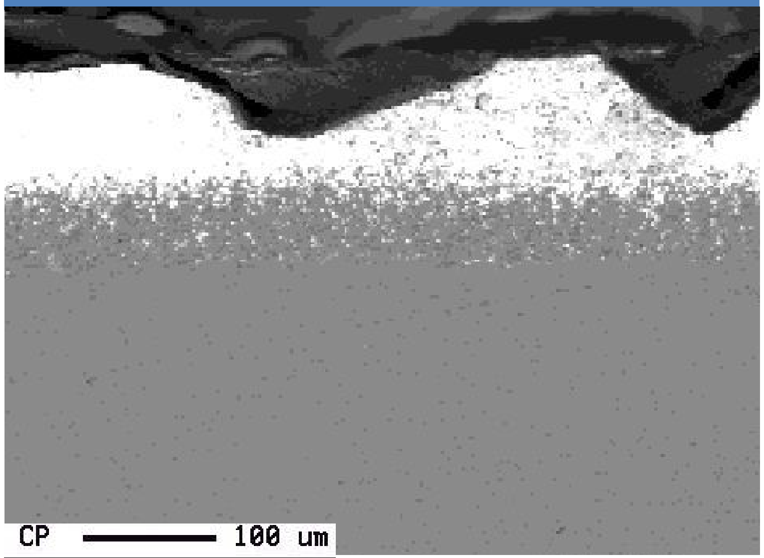


PM2000 (20Cr, 5.5Al, 0.5Y_2O_3)

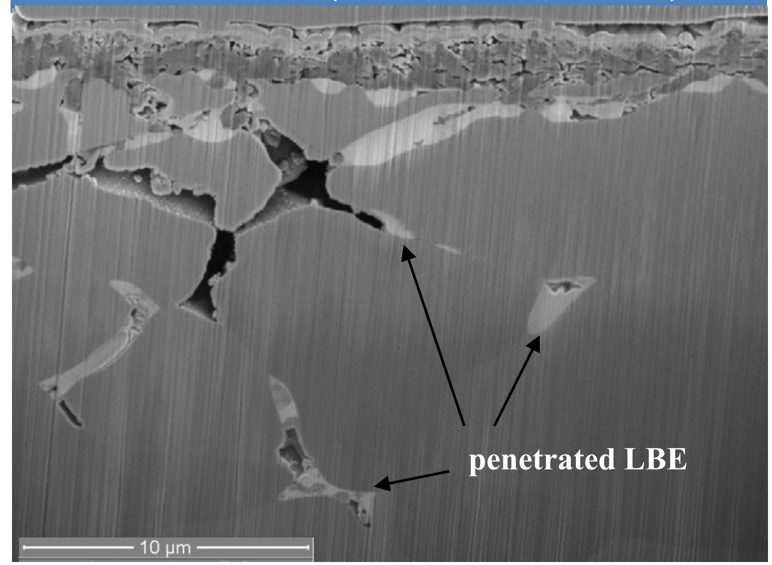


Results : 550°C for 500hrs

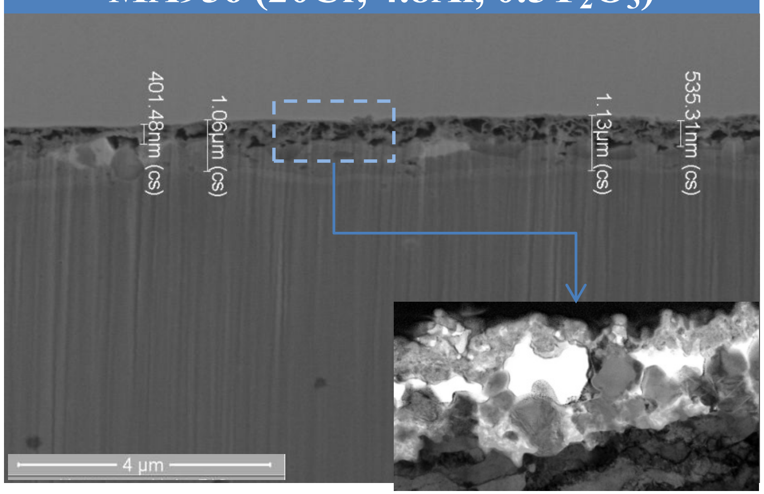
SS316L



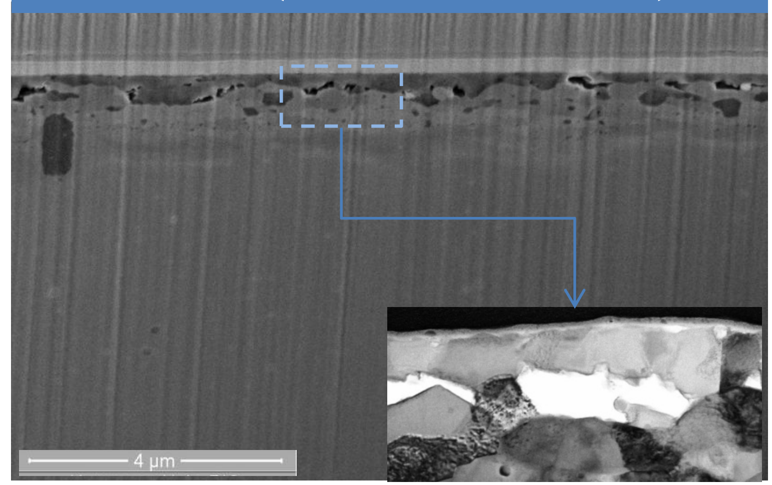
Kanthal-AF (22Cr, 5.3Al, 0.03Y)



MA956 (20Cr, 4.8Al, 0.5Y_2O_3)

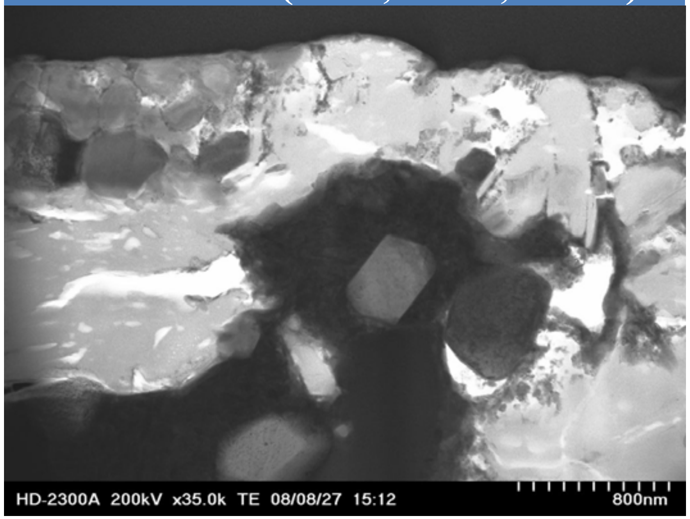


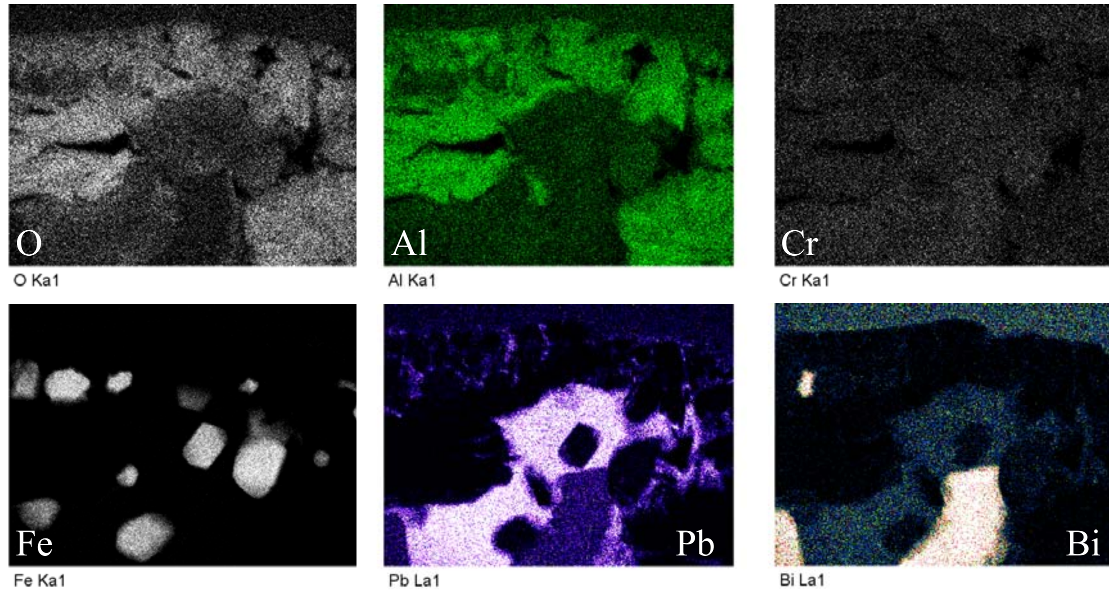
PM2000 (20Cr, 5.5Al, 0.5Y_2O_3)



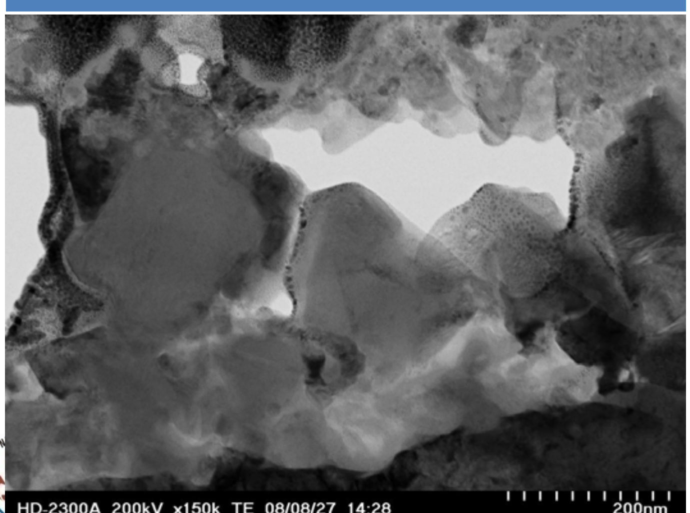
Results : STEM images and EDS analysis (550^{o}C results)

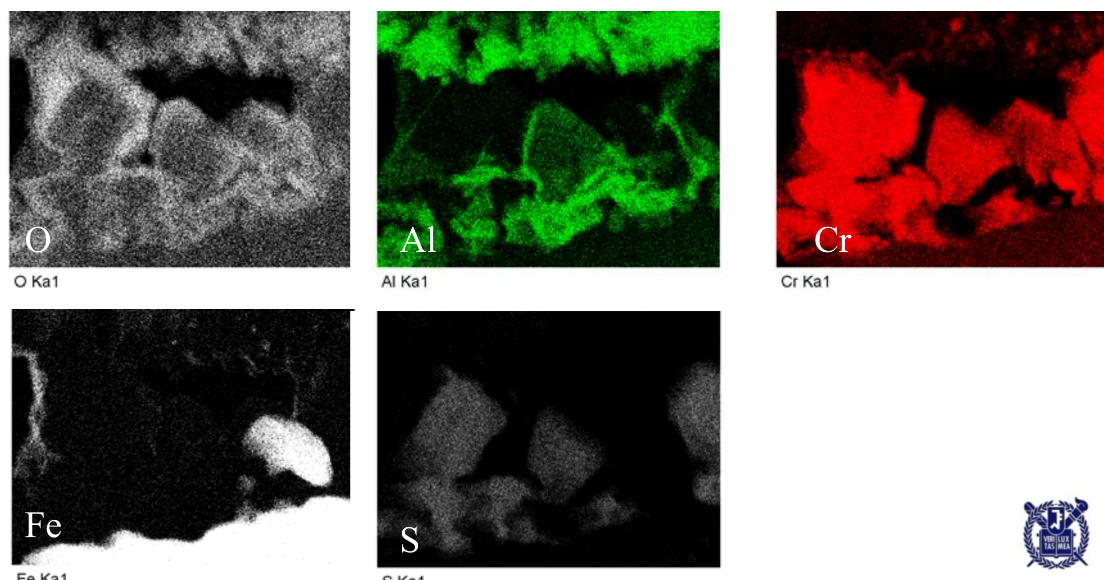
Kanthal-AF (22Cr, 5.3Al, 0.03Y)





MA956 (20Cr, 4.8Al, 0.5Y_2O_3)





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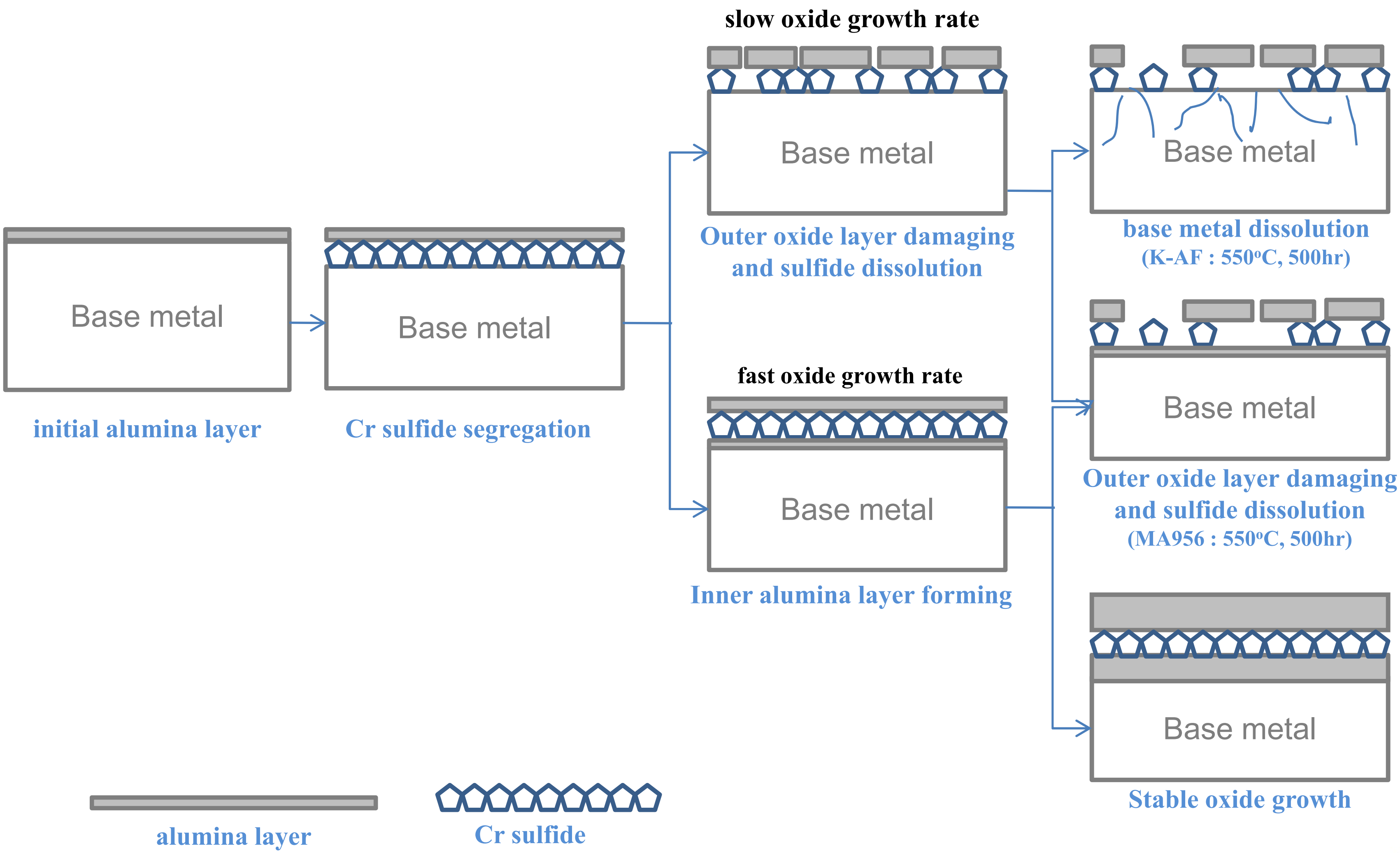
Oxide growth and dissolution mechanism of commercial FeCrAl alloys in LBE



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Summary and future work

- Based on test and model, the total oxide thickness of FMS steels was predicted at 450^{o}C. HT-9 appears to be acceptable cladding for PEACER, but not for PASCAR.
- Corrosion behaviors of alumina forming alloys and conventional FeCr alloys have been investigated in static and flowing LBE.
- Bulk concentration of sulfur ranged from one-tenth ppm to a few ppm in investigated FeCrAl alloys. Even at such low levels, S segregated strongly to Al_2O_3/alloy interface, forming Cr sulfide.
- The formation of Cr sulfide appears to promote void formations at the oxide/alloy interface, weakening the interfacial bonding and leading to severe dissolution attack in LBE.
- Wall thinning model for magnetite layer and means for the suppression of S segregation in Al-containing alloys are to be studied in the future.

Acknowledgments

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Thank you for your attention!!