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The effect of hydrogen annealing on the corrosion behaviors of FeCrAl alloy(Kanthal-AF) and SS316L in LBE

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  - Oxide growth mechanism of FeCrAl alloy in LBE when affected S segregation
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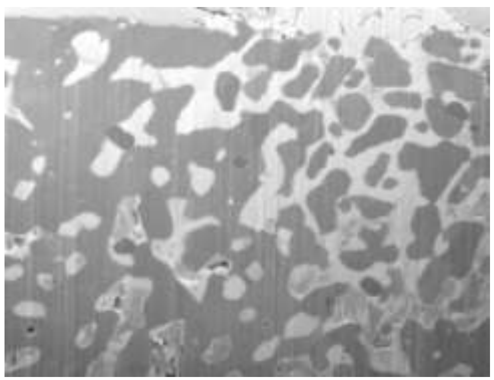
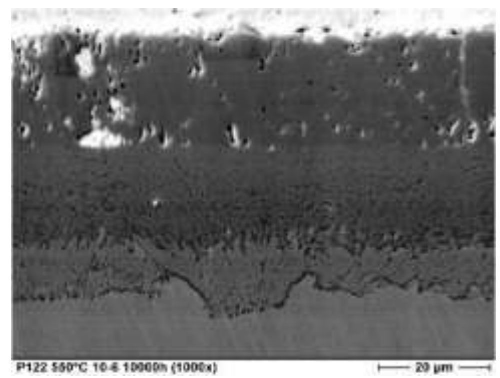
Introduction

- Austenitic SS and ferritic/martensitic steels (HT9, T91) have shown relatively good corrosion resistance in LBE at controlled oxygen levels (>10^{-7}wt%) in the temperature range of 300°C~470°C
- Because of the severe dissolution or fast oxide growth at high temperature (>500℃) in case of conventional FeCr- alloys (SS316L, HT9, T91..) in LBE, better materials are needed.



Dissolution attack



Oxidation damage

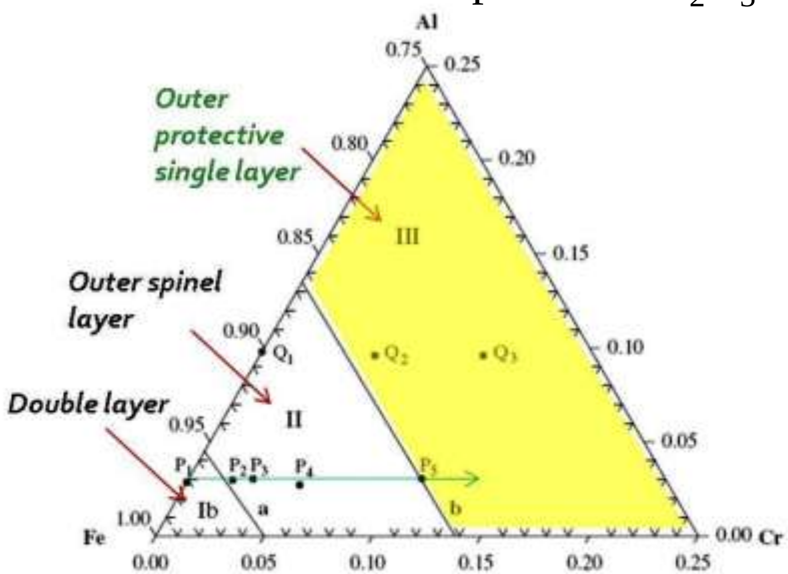
- For high temperature (>500°C) applications, Al-containing alloy and Al-coated steels (GESA treatment by FZK) have shown promise in addition to Russian Si-containing alloys.

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)
  - Cr serves to promote Al_2O_3 formation.



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.

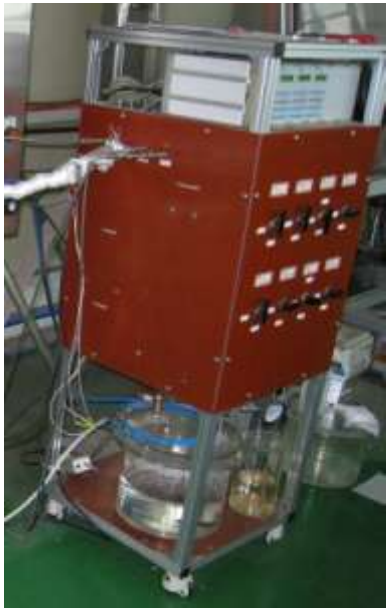
Literature Review - Oxidation of FeCrAl alloys

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

- Sulfur segregation at thermally grown Al_2O_3/alloy interface
  - During high temperature oxidation of alumina forming alloys, Sulfur in the alloy consistently segregate at the Al_2O_3/alloy interface; Its presence weakens the interfacial bonding of oxide and may disturb the stable growth of Al_2O_3
  - Where Cr is present, Cr can enhance S segregation to the interface due to co-segregation effect.
  - The segregation of sulfur tends to vary with time and temperature owing to the dynamic nature of the oxidation process.

Experimental - Materials and Apparatus

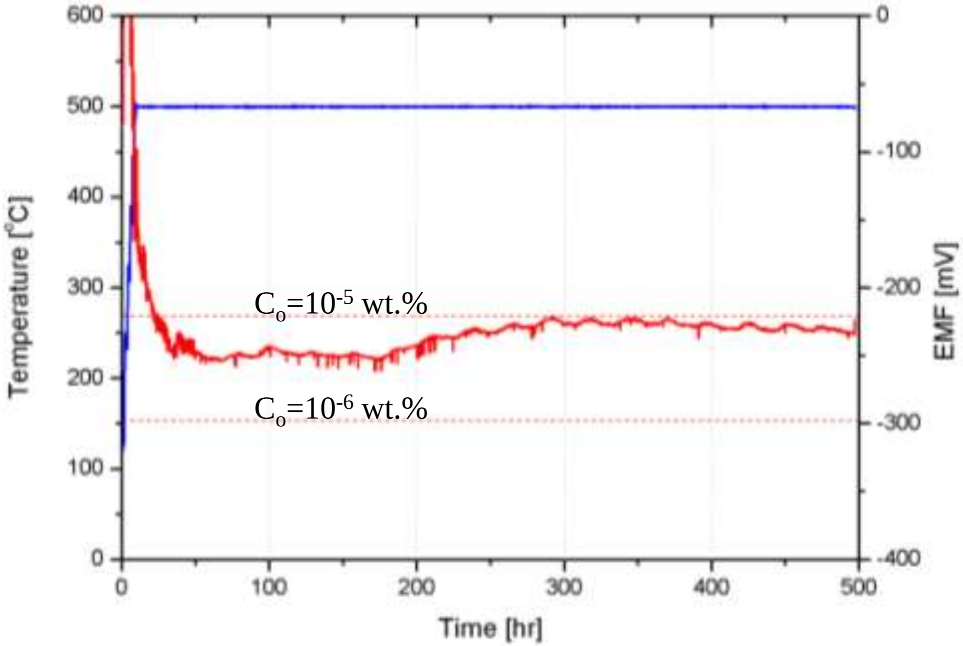
Material	Fe	Cr	Ni	Al	Si	Mn	Mo	S	Ti	V	Y	Zr	
SS316L	Bal.	16.5	10.1	-	0.35	1.8	2.31	0.008	-	-	-	-	*SS*
T91	Bal.	8.6	0.23	-	0.3	0.43	0.95	0.006	0.003	0.2	-	-	*FMS*
Kanthal-AF	Bal.	22	-	5.1	0.21	0.17	-	0.004	0.07	-	0.03	0.08	FeCrAlY



Photograph of static cells (left) and oxygen control system (right)

Experimental –Test Conditions

Specimen and Conditions	
Specimen type (size)	Sheet (25x 8x1 mm)
Surface treatment	Polished by SiC paper up to 600grit
LBE container	Alumina crucible
LBE quantity	10kg
Test Temperature	450ºC~650℃
Oxygen in LBE	10^{-7} ~ 10^{-5} wt%
Oxygen control	Mixture of H_2/H_2O gas
Oxygen sensor	YSZ with Bi/Bi_2O_3
Method s of analysis	
FIB-FESEM, STEM, EDS, EPMA	

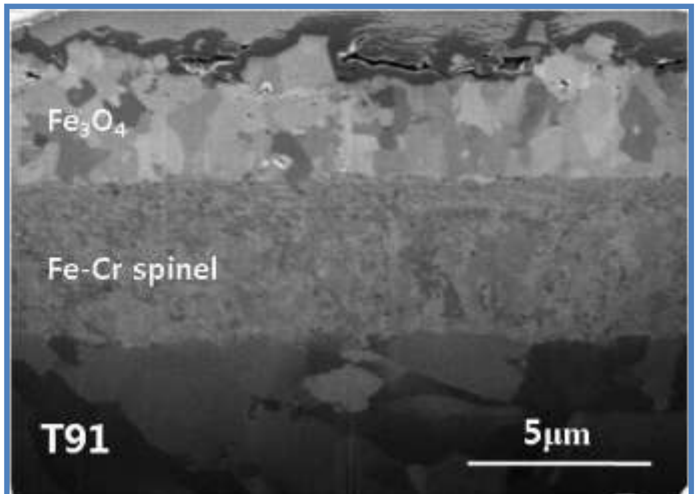


Measured Temperature and Oxygen Potential

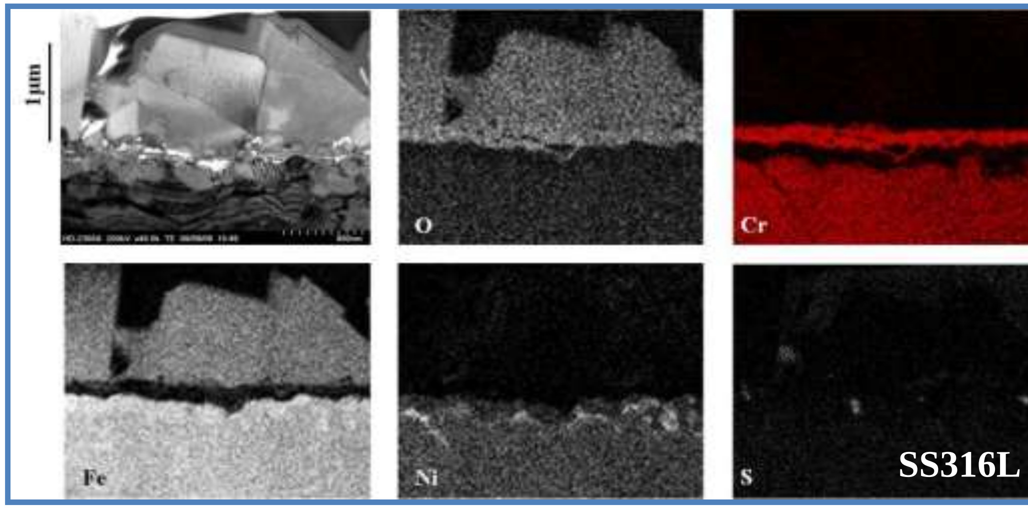
- Blue line : Temperature , Red line : Oxygen potential

Results – 500^oC for 500hrs, $C_o=10^{-6}\sim10^{-5}wt\%$

condition	T91	SS316L	Kanthal-AF
500^{o}C 500hrs			

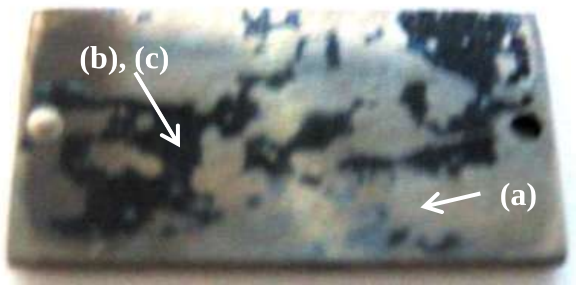


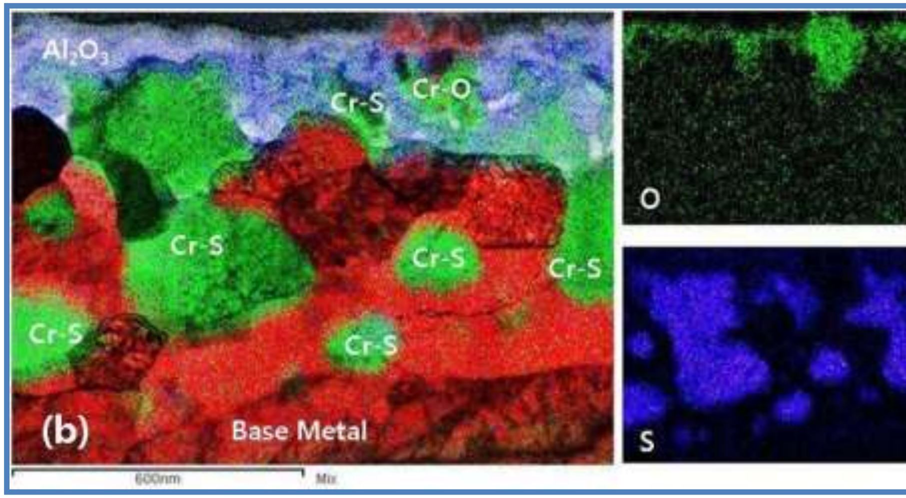
Cross Section of T91 : FIB Image

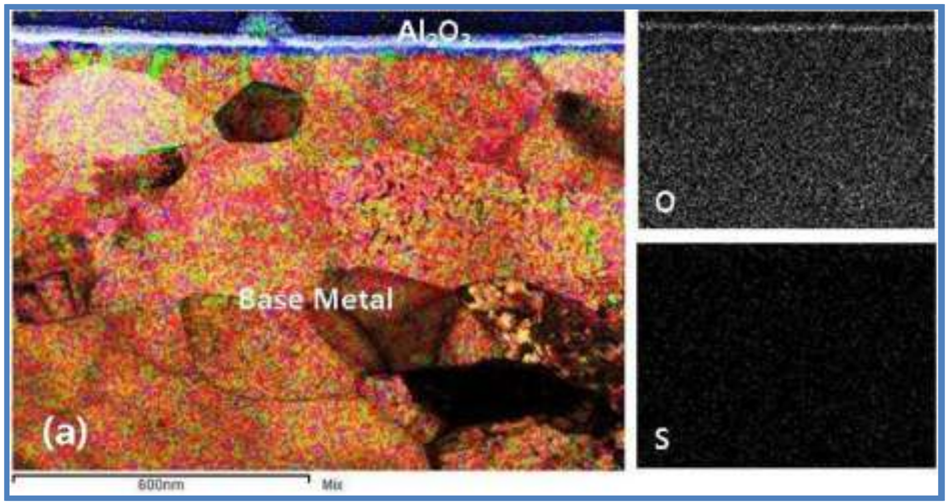


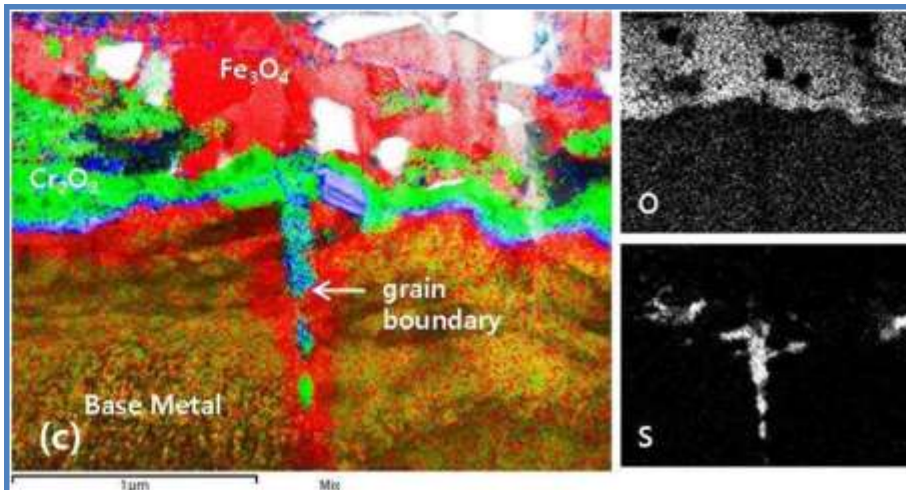
Cross Section of SS316L : STEM, EDS mapping

Results – Kanthal-AF (500^{o}C for 500hrs.)



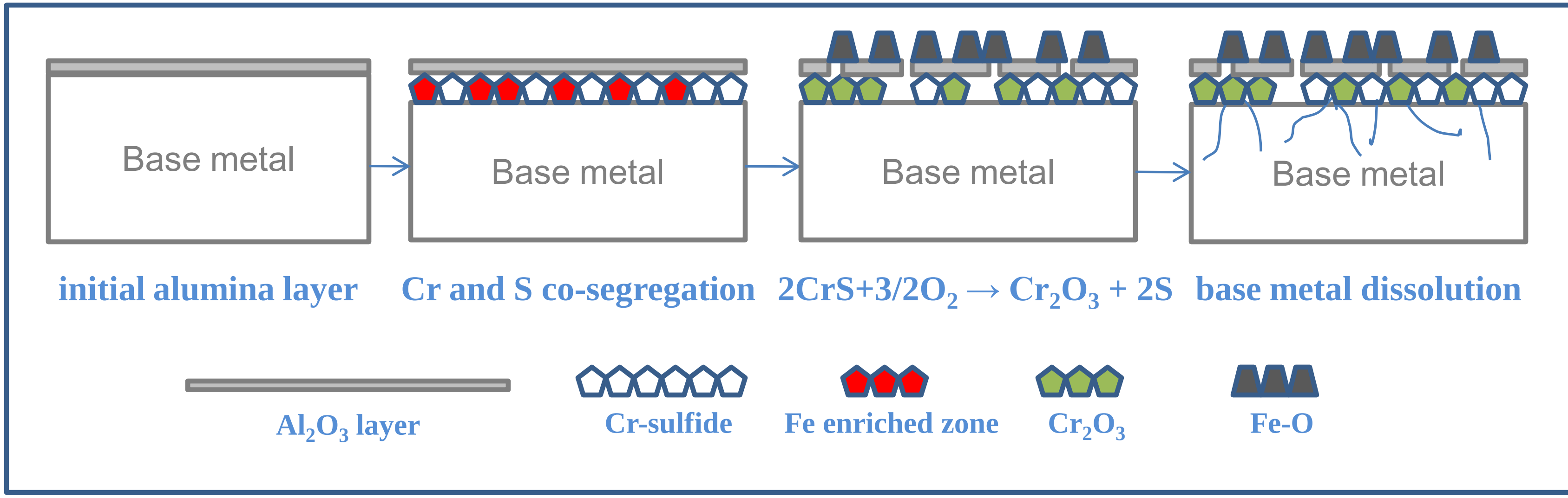




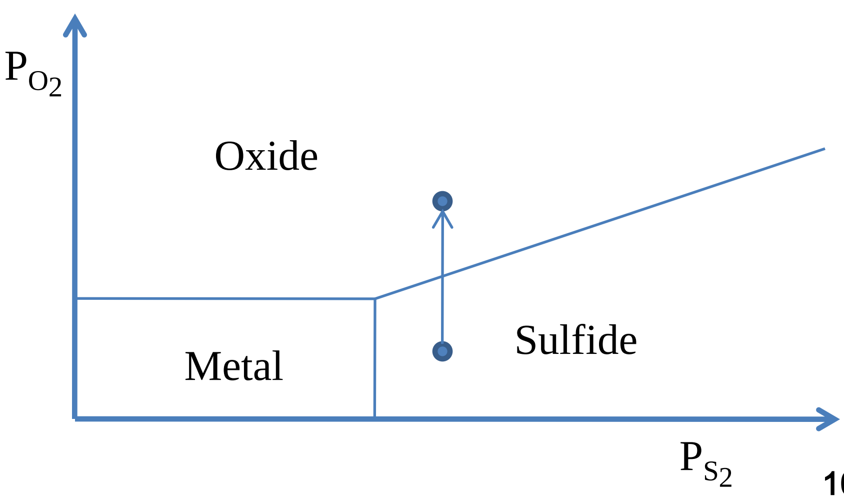


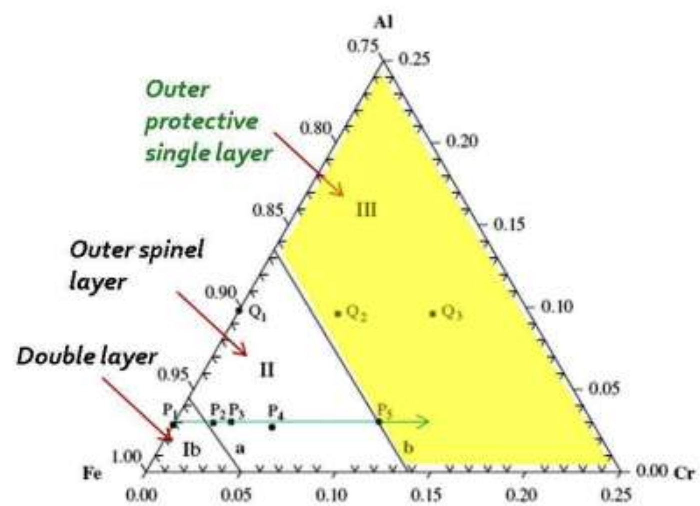
Cross sections of Kanthal-AF : STEM, EDS mapping
(Red : Fe, Green: Cr, Blue : Al in the coupled composition images)

Oxide growth mechanism of FeCrAl alloy in LBE when affected S segregation



※ **Pilling-Bedworth ratio - Cr_2O_3 : 2.07, CrS : 2.50**





Hydrogen annealing heat treatment

- Purpose
  - Reduce sulfur content in the alloys
  - $S + H_2 = H_2S(g)\uparrow$

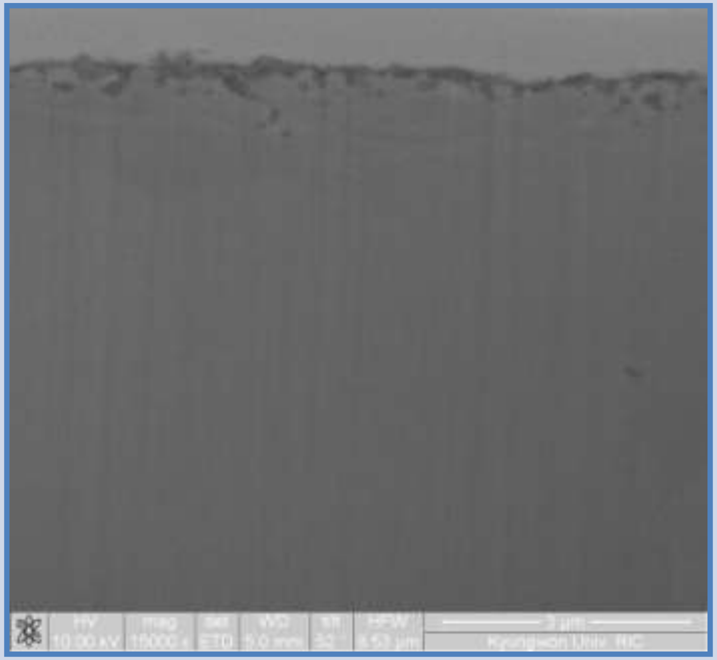
- Heat treatment condition
  - Temperature : 1200^{o}C
  - flowing 99.99wt.% H_2
  - duration : 100hrs
  - cooling by flowing Ar gas

- Materials - Kanthal-AF, SS316L
  - SS316L : γ phase → $\gamma + \delta$ phase

- The S levels in hydrogen annealed alloys reduced down to 1ppmw.

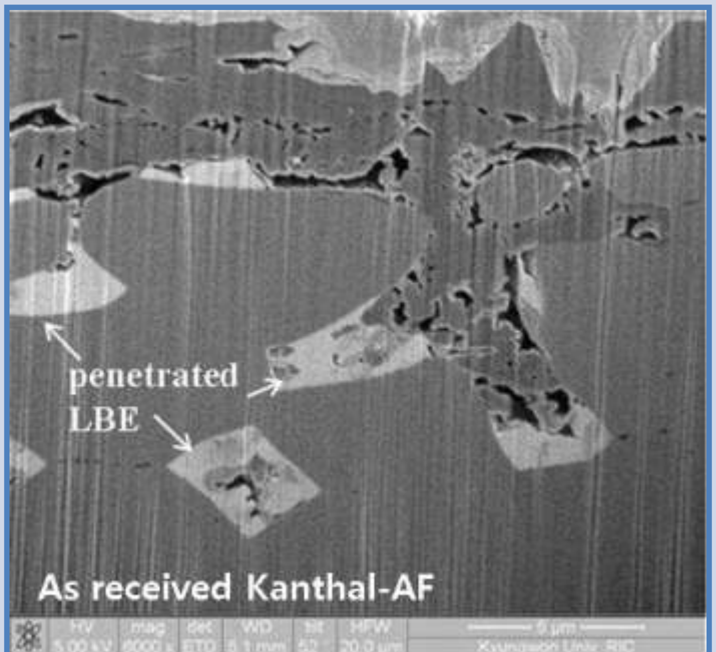
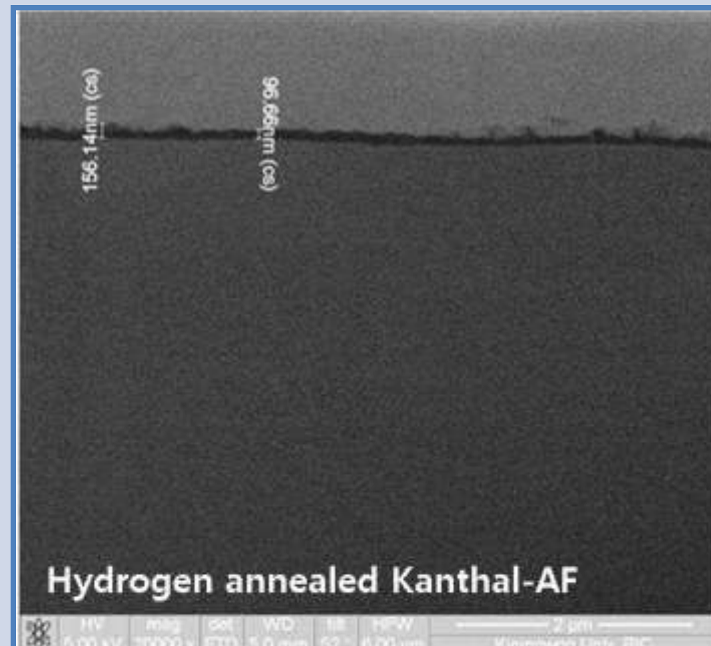
Results : Kanthal-AF with and without heat treatment

- 550^{o}C for 100hrs, Co=10^{-7}wt.%

condition	As received Kanthal-AF	Hydrogen annealed Kanthal-AF
Surface		
SEM image of cross section		

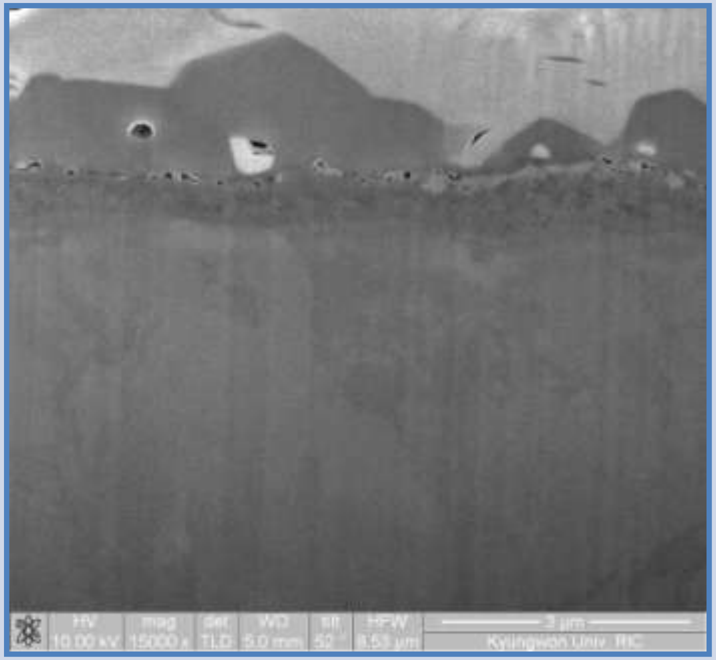
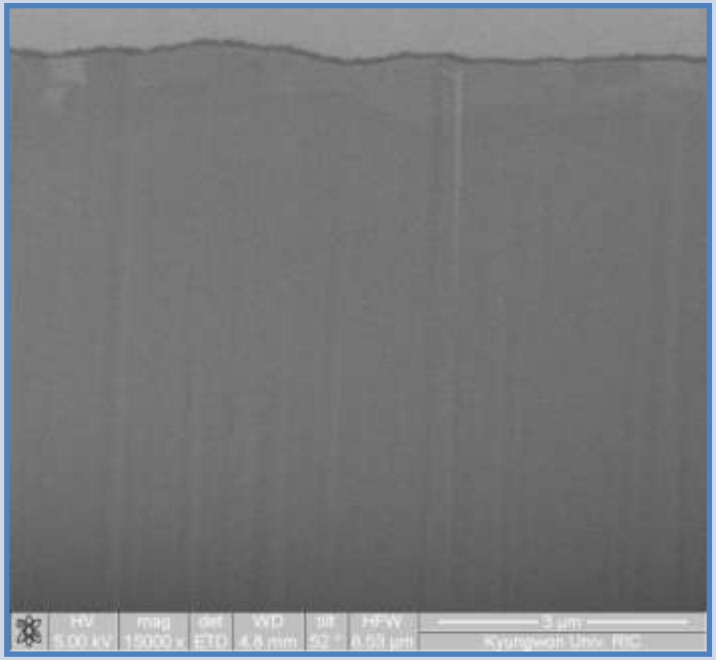
Results : Kanthal-AF with and without heat treatment

- 650°C for 500hrs, Co=10^{-6}wt.%

condition	As received Kanthal-AF	Hydrogen annealed Kanthal-AF
Surface		
SEM image of cross section		

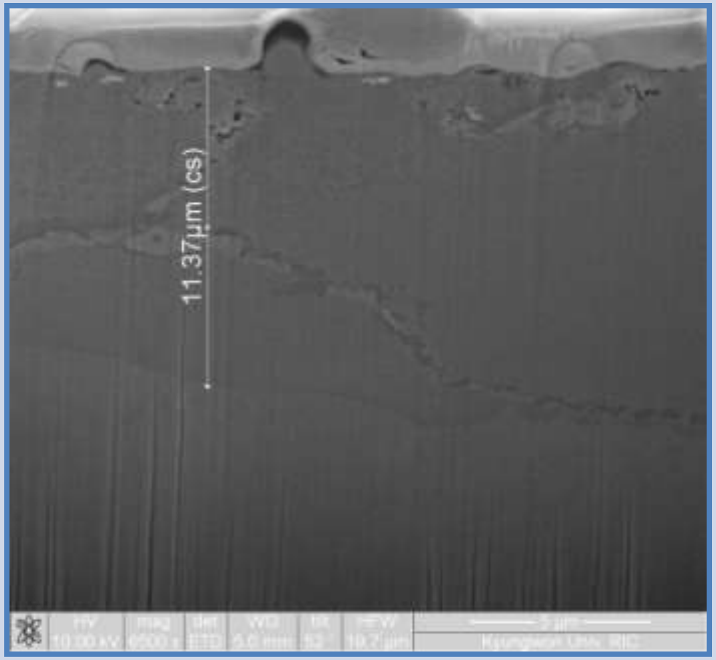
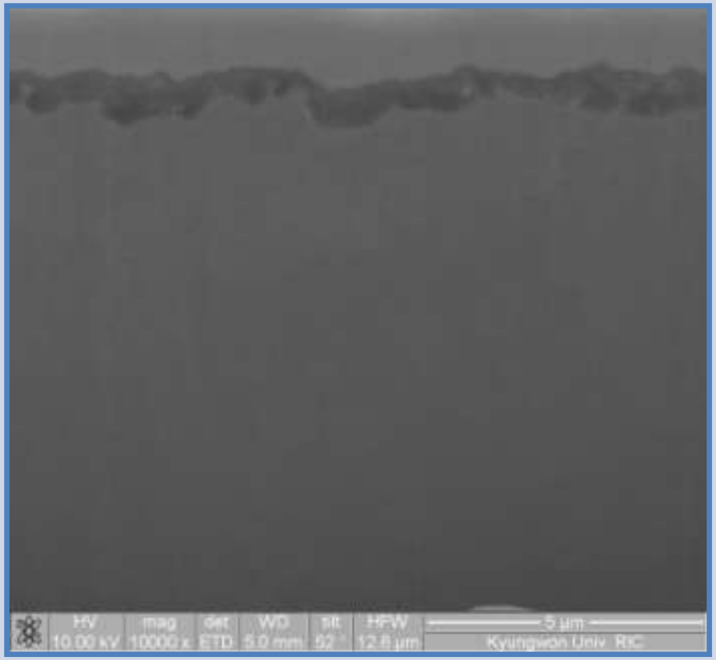
Results : SS316L with and without heat treatment

- 550^{o}C for 100hrs, Co=10^{-7}wt.%

condition	As received SS316L	Hydrogen annealed SS316L
Surface		
SEM image of cross section		

Results : SS316L with and without heat treatment

- 600°C for 1000hrs, Co=10^{-6}wt.%

condition	As received SS316L	Hydrogen annealed SS316L
Surface		
SEM image of cross section		

Summary and future work

- Corrosion behaviors of Kanthal-AF and SS316L with and without hydrogen annealing heat treatment have been investigated in stagnant LBE

- Analysis results show that the H_2 annealing heat treatment improve corrosion resistance under the LBE condition for both Kanthal-AF and SS316L

- More detail analysis of H_2 annealing heat treatment materials are to be studied. (chemical composition, TEM analysis of oxide layer, microstructure)

- Low S alloys will be made and tested in the near future.

Acknowledgments

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Thank you for your attention!!