Development of FeCrAl alloys for ATF cladding materials

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Workshop : 최신 핵연료 및 원자력재료 연구 개발 현황

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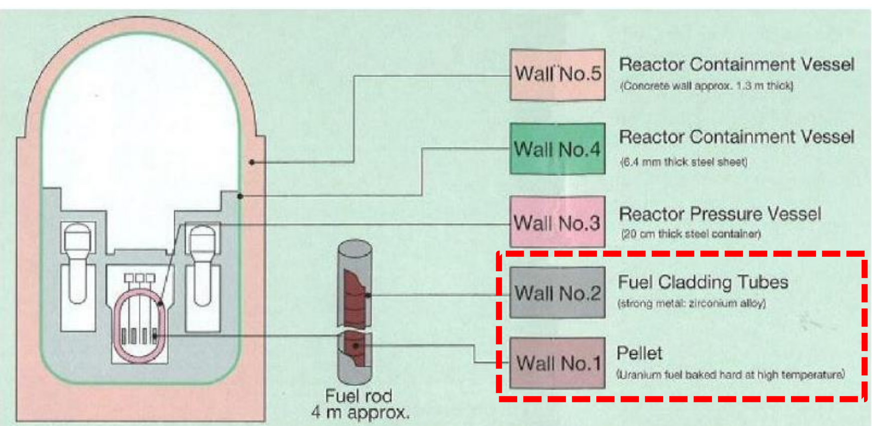
- Background
- Alloy fabrication
- High temperature oxidation resistance
- Corrosion test in PWR environment
- Tensile test
- Summary

Background

▪ Zirconium cladding

- ✓ Good corrosion resistance in the operating environments of light water reactor.
- ✓ Rapid oxidation reaction occurs when the loss-of-coolant accident (LOCA) occurs as in the Fukushima nuclear power plant accident.
- ✓ If the hydrogen generated by this oxidation reaction accumulates inside the containment, hydrogen explosion may occur.

$$Zr + 2H_2O \rightarrow ZrO_2 + 2H_2$$



The role of nuclear fuel and nuclear fuel cladding in multiple firewalls

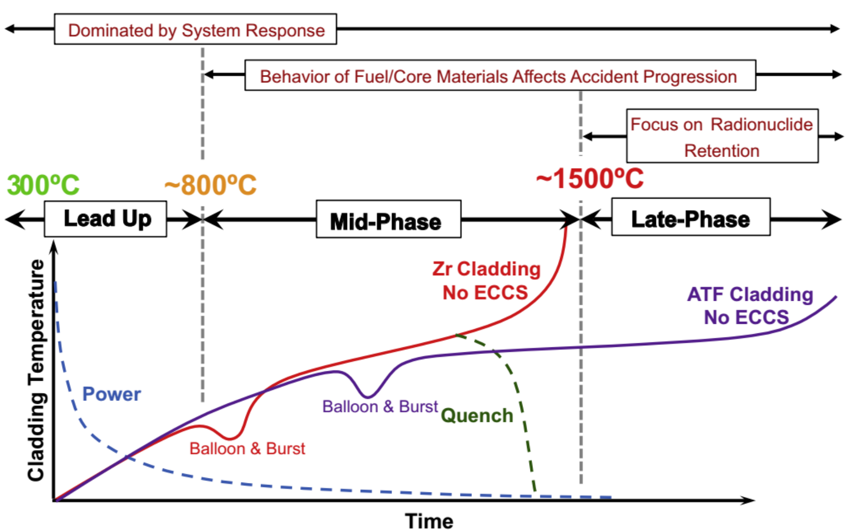
(Left) High-temperature oxidation behavior of zirconium alloy cladding, (right) Picture of a nuclear accident with hydrogen explosion after LOCA

Background

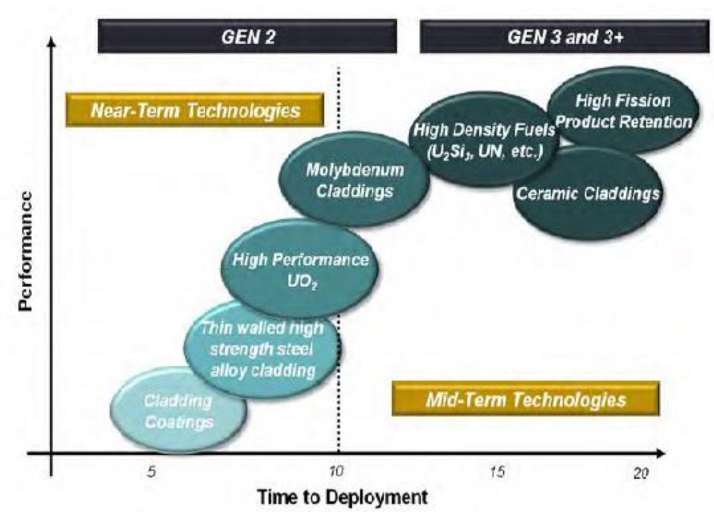
▪ Accident-tolerant Fuel (ATF) Cladding

✓ It is necessary to develop ATF cladding with **low oxidation rate** and **low hydrogen generation** even at the LOCA.

- ***Short-Term*** : Coating technology applied to the surface of zirconium alloys.
- ***Long-Term*** : It is necessary to develop new alloys that completely replace the zirconium alloys.



General overview of coolant–limited accident progression inside an LWR core.



Comparison of major accident tolerant fuel concepts

Zinkle, Steven J., et al. "Accident tolerant fuels for LWRs: A perspective." *Journal of Nuclear Materials* 448.1 (2014): 374-379.
A.G. SOWDER. "Challenges and Opportunities for Commercialization of Enhanced Accident Tolerant Fuel for Light Water Reactors : Utility-Informed Perspective." IAEA-TECDOC-1797. 119-127.

Background

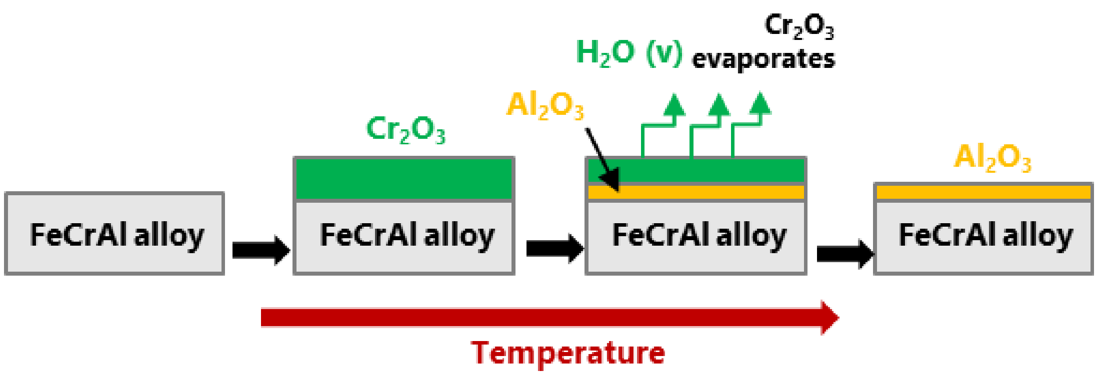
The FeCrAl alloys

✓ Advantage

- High temperature oxidation resistance.
- Resistance to corrosion under primary water environments.
- Hydrogen embrittlement ↓
- Do not need coating, bonding technology.
- Commercialized material as electric heating wire.

✓ Disadvantage

- '475 °C embrittlement'
  Phase separation under 500℃
  - α-(Fe, Cr) ferrite
  - Cr-rich ferrite (α')
- Al content ↑, Fabricability ↓
- Neutron absorption cross section is 10 times higher than Zr.



Corrosion behavior of FeCrAl alloys

Background

- **Research outline**

Fe-Cr-Al base alloy

Alloy design

- Chemical composition
- Manufacturing process
- Microstructure

Oxidation resistance

- **1200℃ steam/Ar**
- **PWR water chemistry**

Mechanical property

- **Tensile property**
- **Machinability**
- **Fracture toughness**

Background

- **Yttrium addition**
  - ✓ Increase the high temperature oxidation resistance.
  - ✓ Prevent the aluminum oxide spallation during air quenching.
  - ✓ Reduce the grain size.

But..

- **Optimized yttrium contents ?**
- **Yttrium behavior under 1200℃ ?**
- **What mechanism does it follow ?**

Still unclear.

General Electric	
Fe-5Cr-6Al-1Y	Fe-25Cr-4Al
Fe-5Cr-6Al-1Y-3Mo	Fe-25Cr-4Al-1Y-1Nb
Fe-10Cr-4Al-1Y	Fe-25Cr-4Al-1Y
Fe-10Cr-6Al-1Y	Fe-5Cr-6Al-1Nb
Fe-15Cr-4Al	Fe-5Cr-6Al-3Y
Fe-15Cr-4Al-1Y	Fe-5Cr-7Al-1.5Y
Fe-25Cr-4Al-0.35Y	Fe-13Cr-6Al-1.5Y
Fe-25Cr-3Al-0.5Y	

Oak Ridge National Laboratory
Fe-15Cr-5Al-0.05Y
Fe-15Cr-5Al-0.15Y
Fe-13Cr-5Al-2Mo-0.2Si-0.05Y
Fe-13Cr-5Al-2Mo-1Nb-0.2Si-0.05Y
Fe-13Cr-7Al-2Mo-0.2Si-0.05Y
Fe-10Cr-6Al-2Mo-0.2Si-0.05Y
Fe-13Cr-6Al-2Mo-0.2Si-0.05Y

Alloy fabrication

Alloy designation and chemical composition

- ✓ Based on Fe-13Cr-6Al, Y free alloy was named as 136.
- ✓ Y doped alloys were named as 136Y-1, 136Y-2 and 136Y-3 in order of increasing Y content.

Alloy Designation	Nominal composition	Analyzed Y wt.%
144	Fe-14Cr-4Al	-
136	Fe-13Cr-6Al	-
144Y-2	Fe-14Cr-4Al-**0.3Y**	**0.149**
136Y-1	Fe-13Cr-6Al-**0.15Y**	**0.032**
136Y-2	Fe-13Cr-6Al-**0.3Y**	**0.143**
136Y-3	Fe-13Cr-6Al-**0.45Y**	**0.268**

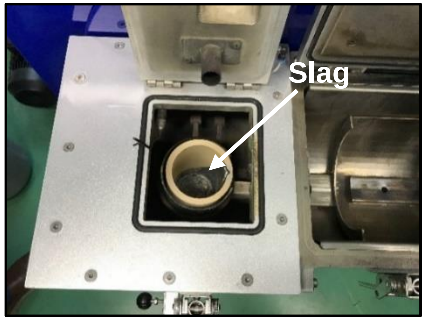
Alloy fabrication

▪ Melting process

Arc melting

Slag form on the surface

Induction melting



Filtered slag after induction melting

Final ingot

Final ingot
(arc melting + induction melting)

▪ Rolling & Heat treatment

Ingot Sample

24.8 T

55 X 100 X 24.8 mm

Homogenized
1200 ℃, 2 hr

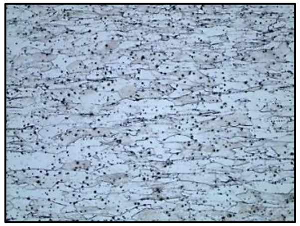
24.8 T

55 X 100 X 24.8 mm

Hot rolling
keep 800 ℃, then Hot rolling

3 T

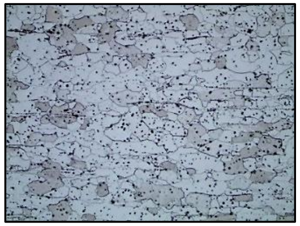
65 X 565 X 3 mm



Annealing
700 ℃, 1hr

3 T

65 X 565 X 3 mm



136Y-2 alloy

High temperature oxidation resistance

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▪ Experimental method

✓ Sample :

- **136, 136Y-1, 136Y-2, 136Y-3**

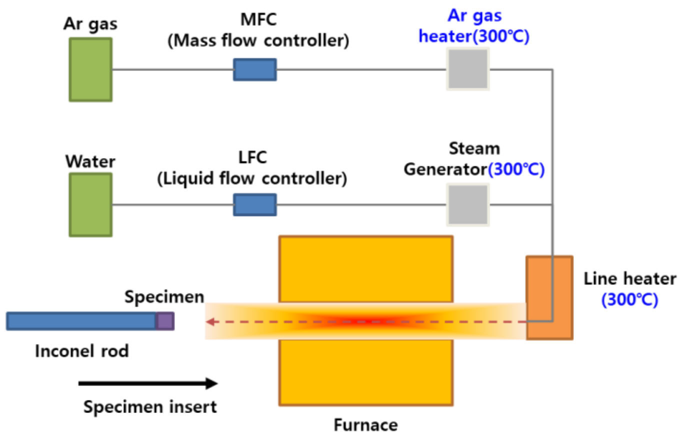
  10x30x2 mm size.

✓ Environment

- 1200 ℃
- Steam and Ar gas at a rate of 500 cc/hr

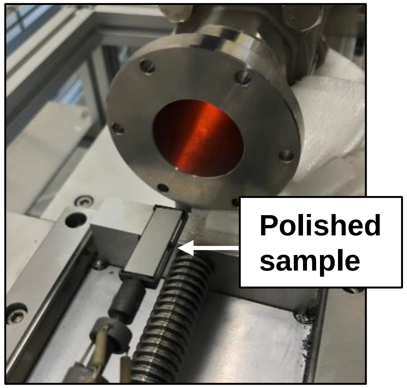
✓ Exposure time :

- 10-min, 3-hr, 8-hr, 24-hr
- After test, oxidized sample was taken out and cooled in air.



A schematic diagram of the experimental set up

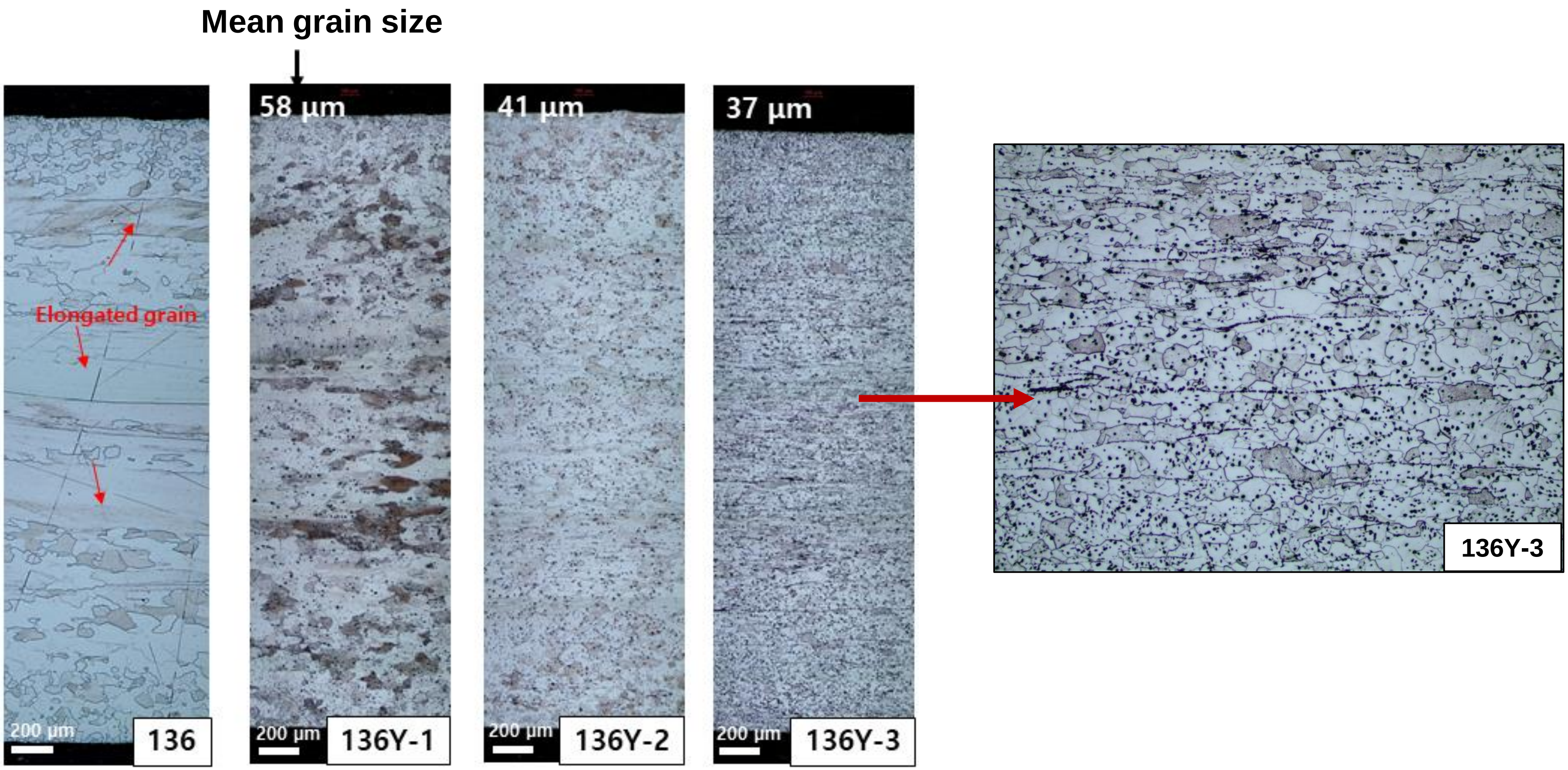
Resistance heating horizontal alumina tube furnace.



The image of our high temperature steam oxidation furnace

High temperature oxidation resistance

- **Grain size and shape**
  - ✓ Non yttrium doped alloy have elongated grain, but not in yttrium doped alloy.
  - ✓ The average grain size of the yttrium doped alloys was about 30 to 60 μm.



Cross sectional optical microscope image(x50) of the FeCrAlY alloy

High temperature oxidation resistance

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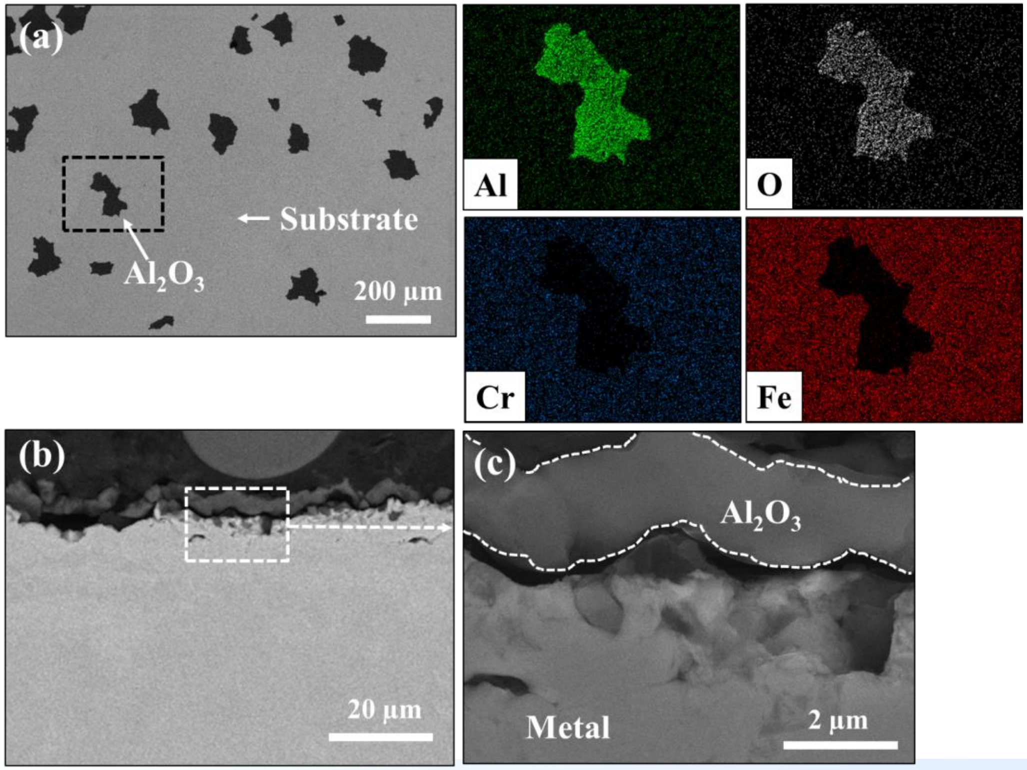
- **Oxide spallation during air quenching**
  - ✓ In the case of non-yttrium doped 136 alloy corroded for 3 hours, <u>most of the aluminum oxide was **spalled out during the air quenching**.</u>
  - ✓ Even the remaining aluminum oxides were **not completely bonded** with the metal substrate and have the <u>**rough metal/oxide and oxide/gas interface**.</u>

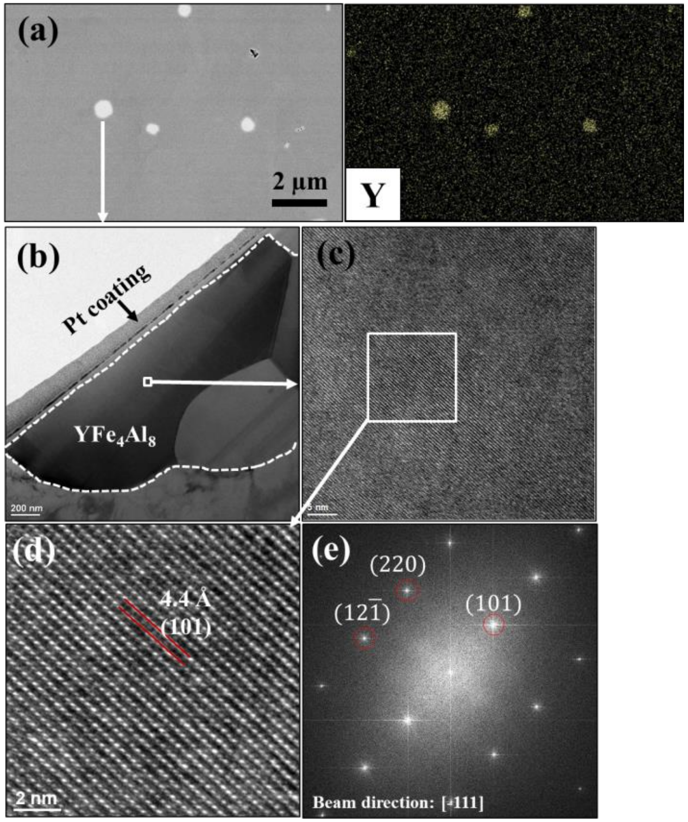
3hours



High temperature oxidation resistance

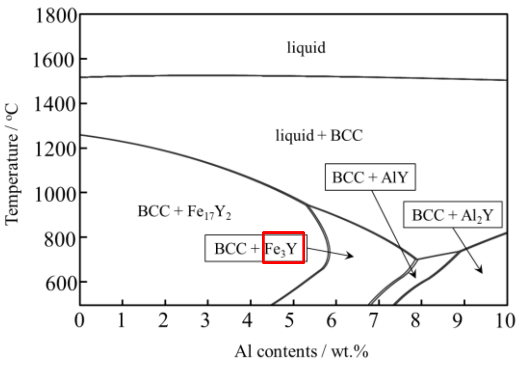
▪ YFe_4Al_8 intermetallic particle

- ✓ YFe_4Al_8 intermetallic particles in tetragonal crystal lattices were uniformly distributed in matrix.
- ✓ EDS results show that Y, Fe and Al were not observed as 1: 4: 8.
- ✓ Al content was relatively much lower than expected.
- ✓ Y is randomly substituted in Al and Fe positions.
- ✓ It seems that YFe_4Al_8 intermetallic particles are formed by combination of Fe_3Y and Fe_3Al.

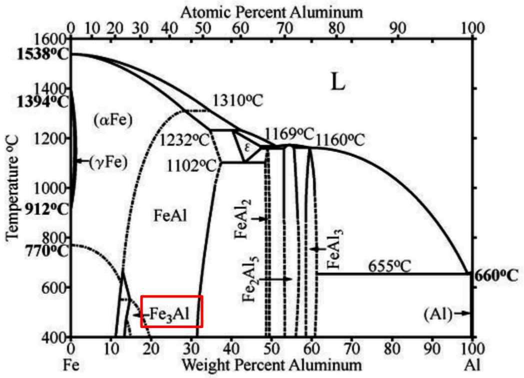


EDS analysis results of YFe_4Al_8 particle.

Element	wt. %	at. %
Y	20.3	70.8
Fe	71.6	12.6
Al	8.1	16.6

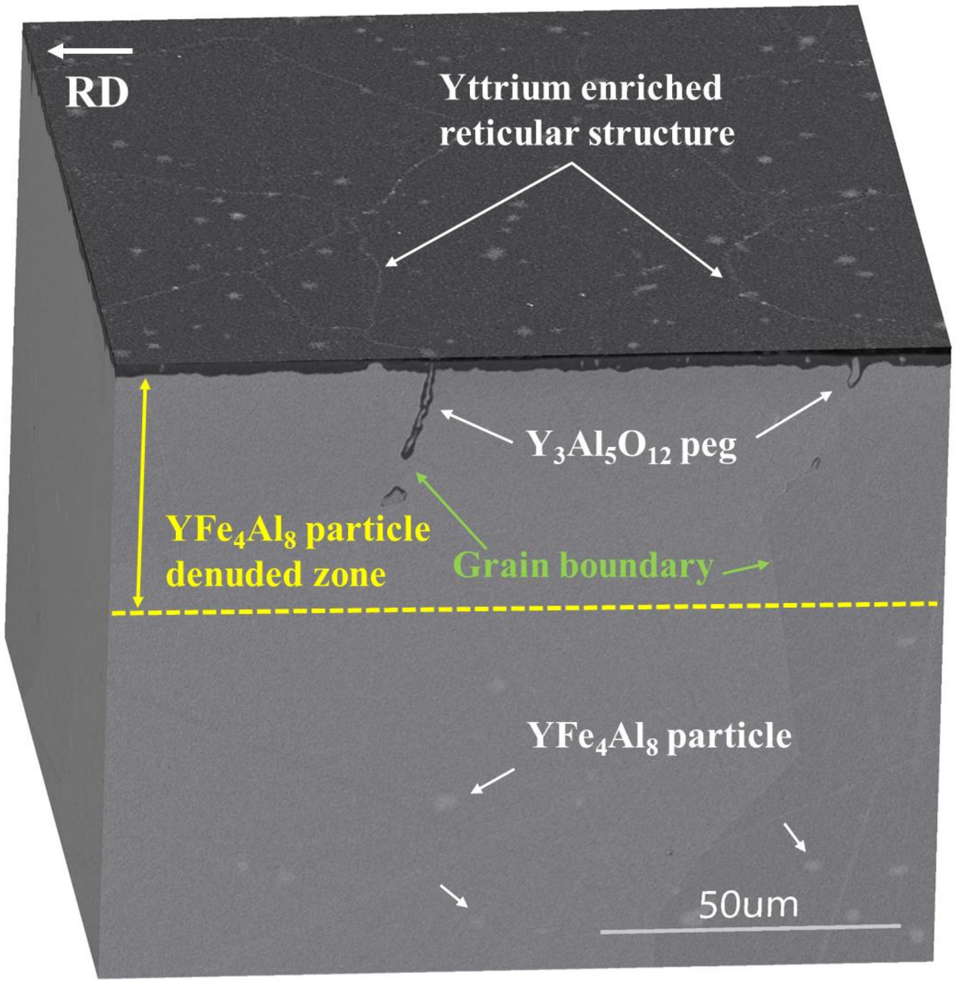


Fe-13Cr-Al-0.15Y phase diagram



Fe-Al binary phase diagram

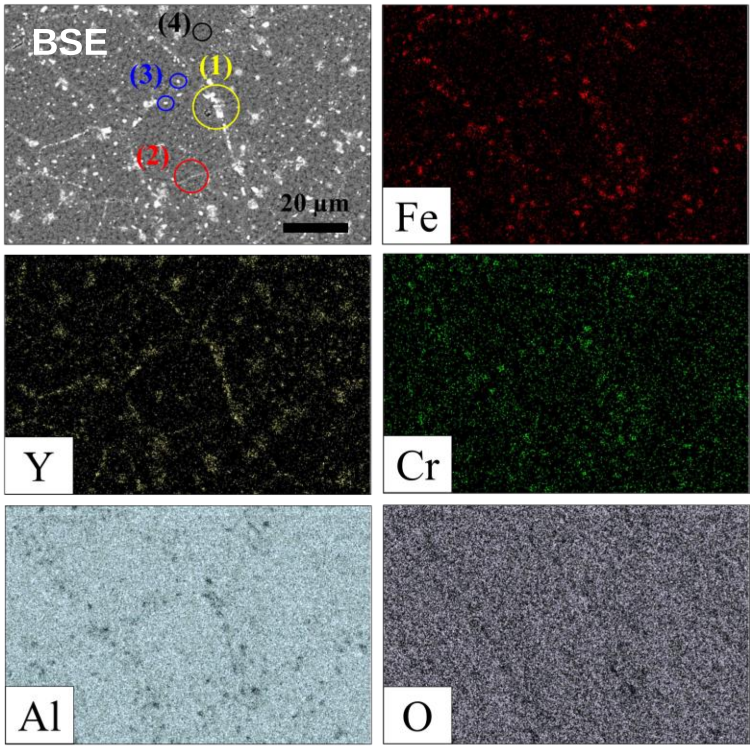
- **Yttrium behavior**



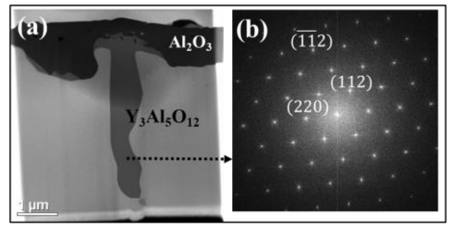
- ✓ No oxide spallation during air quenching
- ✓ Reticular structure
  - The net-like reticular structure formed at the oxidized surface of 136Y alloys.
- ✓ $Y_3Al_5O_{12}$ and Y_2O_3 peg
  - $Y_3Al_5O_{12}$ peg and Y_2O_3 formed at the grain boundary of metal
- ✓ Denuded zone
  - From these formation of peg, ‘Y particle denuded zone’ was formed where Y particles disappeared near the oxidized surface.

High temperature oxidation resistance

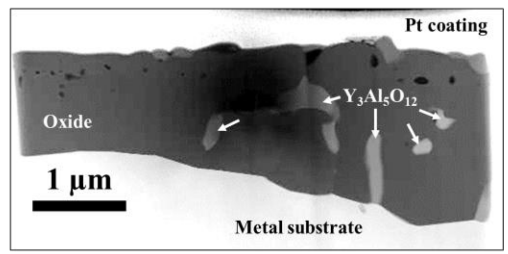
- **Reticular structure with TEM analysis**



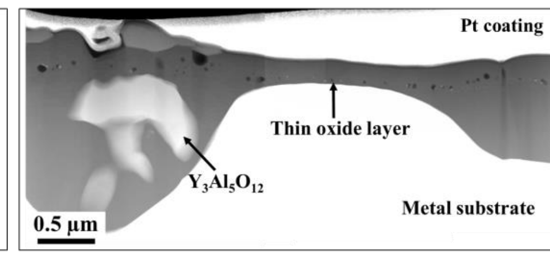
(1) Y rich region with large spot



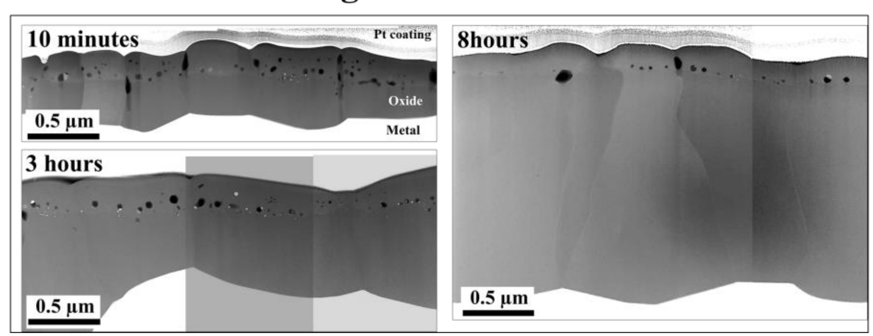
(2) Y rich region with small spot



(3) Fe and Cr rich region



(4) Uniform Al oxide region



✓ The reticular structure has a high Y content.

✓ As the exposure time increased, the grains below this band grew into columnar grain.

High temperature oxidation resistance

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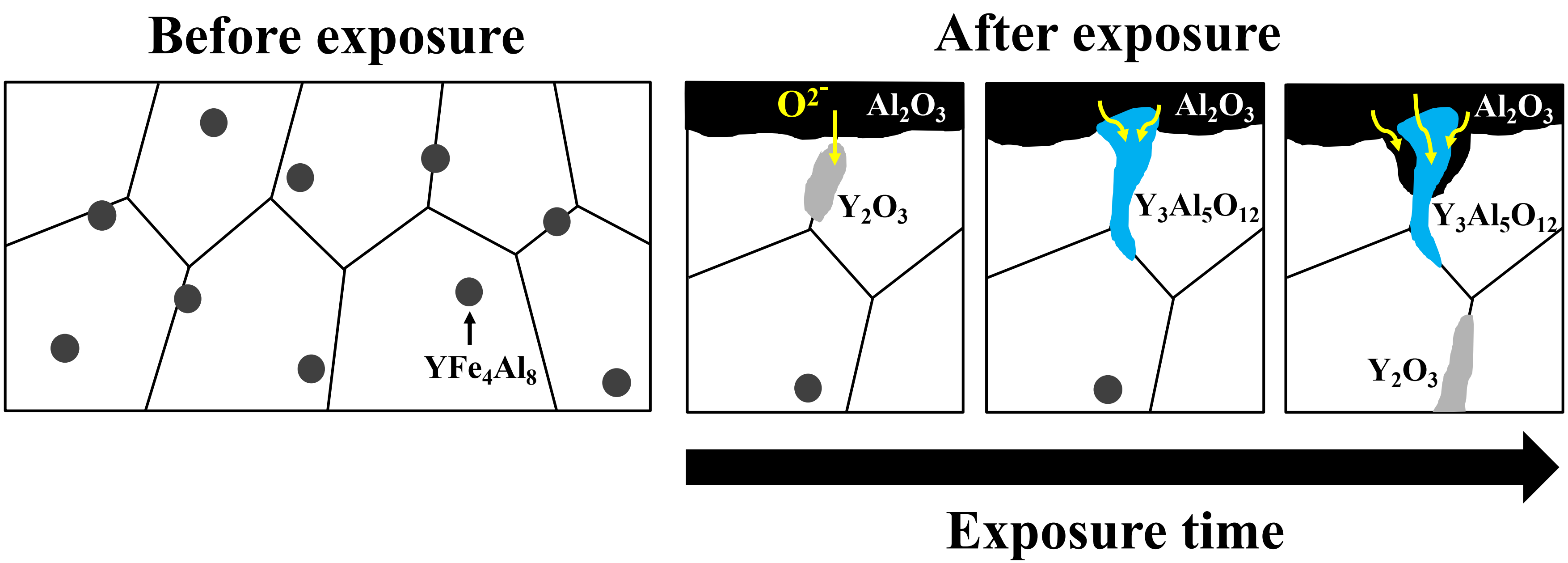
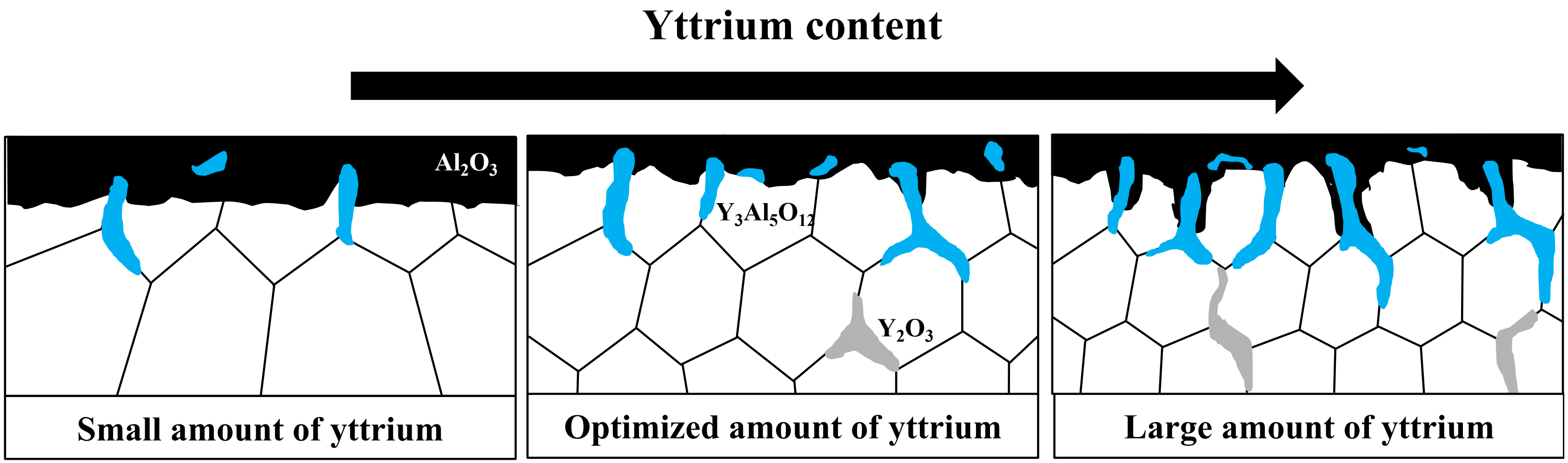


- ✓ YFe_4Al_8 near the surface → Y_2O_3 at metal grain boundary
  Y_2O_3 acts as a short circuit diffusion path for oxygen
- ✓ Al_2O_3 is grew around Y_2O_3, and form $Y_3Al_5O_{12}$ from the reaction of these two compounds.
- ✓ Again, Al_2O_3 is grew around $Y_3Al_5O_{12}$ → Occurring internal oxidation

High temperature oxidation resistance



✓ **Yttrium content ↑** → Number of $Y_3Al_5O_{12}$ peg ↑

↓

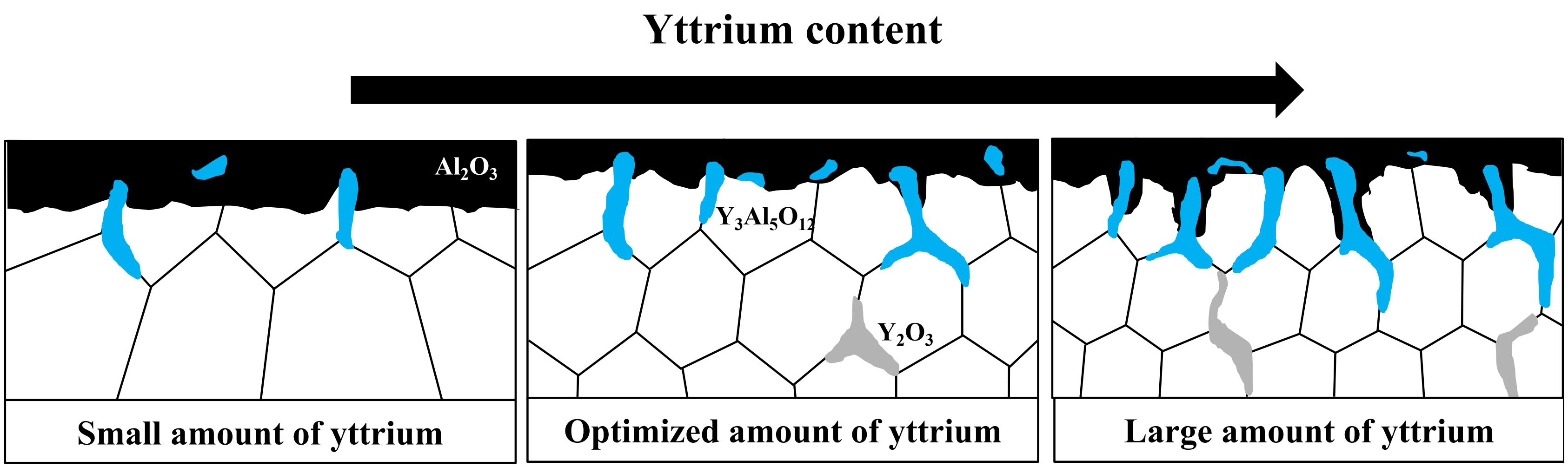
Grain size ↓

↓

Location for formation of $Y_3Al_5O_{12}$ peg

- Accelerate the oxygen diffusion → ***"Negative effect"***
- Internal Al_2O_3

High temperature oxidation resistance



✓ **Yttrium content ↑** ⟶ Number of $Y_3Al_5O_{12}$ peg ↑ ⟶
- Keying effect
- Rough interface

→ Enhance the oxide adhesion

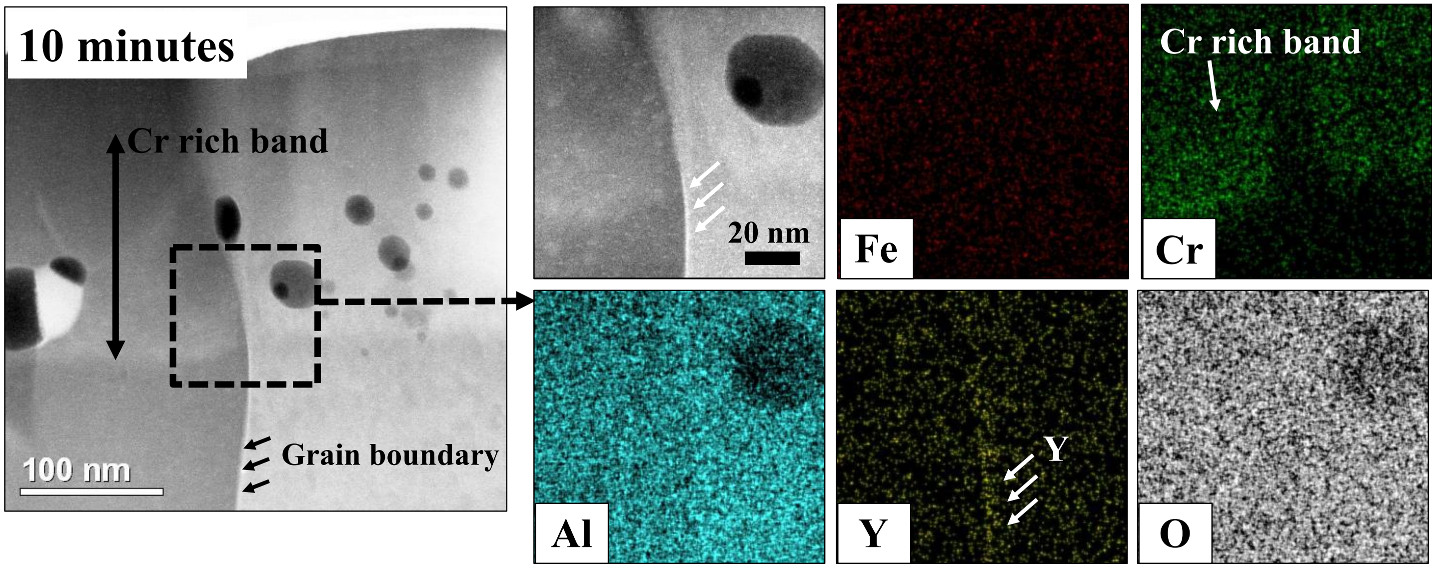
✓ But, It is still questionable how dominant this 'keying effect' to the oxide spallation during the air quenching.

- With 0.032 wt.% Y, oxide spallation didn't occur.
- In ODS FeCrAl alloys (Y added as Y_2O_3), oxide spallation didn't occur.

High temperature oxidation resistance

▪ Yttrium segregation

✓ Y is segregated at the grain boundary of oxide below the Cr rich band.



✓ Prevent the outward diffusion of the aluminum cation.

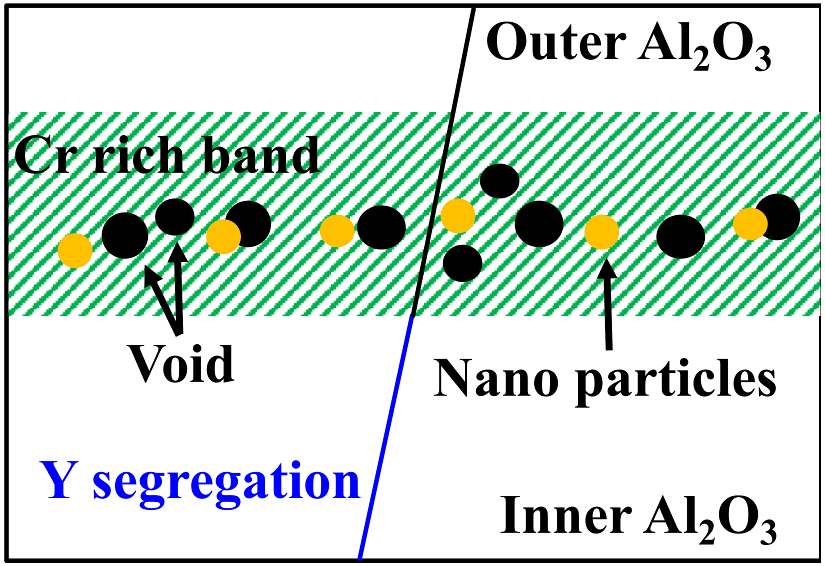
→ Inward diffusion of oxygen ion is dominant.

→ The oxide grows into columnar grain rather than growing in the lateral direction.

→ The oxide layer formed on the non-yttrium doped alloy grows in the lateral direction.

High temperature oxidation resistance

- **Yttrium segregation**



✓ Yttrium segregation

- Inward oxygen diffusion.
- Columnar oxide growth.

✓ Non yttrium segregation

- Inward and outward diffusion.
- Lateral oxide growth.
- Compressive stress

✓ The oxide adherence is considered to be more influenced by Y segregation at the grain boundary of Al oxide than the keying effect by the pegs.

High temperature oxidation resistance

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- **Yttrium segregation**

  ✓ How yttrium segregation change the diffusion process?

Pint et al.

'Blocking'

Ionic radius

Ionic size Hf < Zr < Dy < La [1)]

Oxidation rate Hf > Zr > Dy > La

Li[2)] reported physical ion size has no effect to diffusion process

Effective radius

- Reactive element ions have larger effective radius than their ionic radius[3)].

  → RE may influence the electronic structure and diffusion activation energy of Al ions on the Al_2O_3 grain boundary.

Heuer et al.

- Oxidation continues by: **Mass (ionic species, metal and oxygen)**

  Electronic species (electron and hole)
- **Electronic species will be very important to keep the ion transport going on**.
- RE ions react with electronic species

  → Affect population of electronic species and the **ionic transport**.

High temperature oxidation resistance

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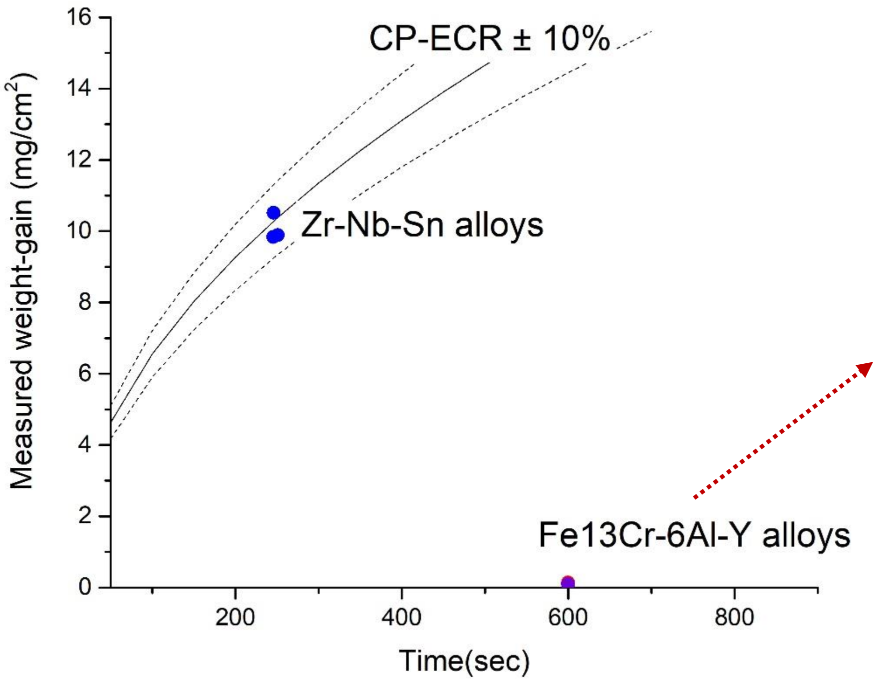
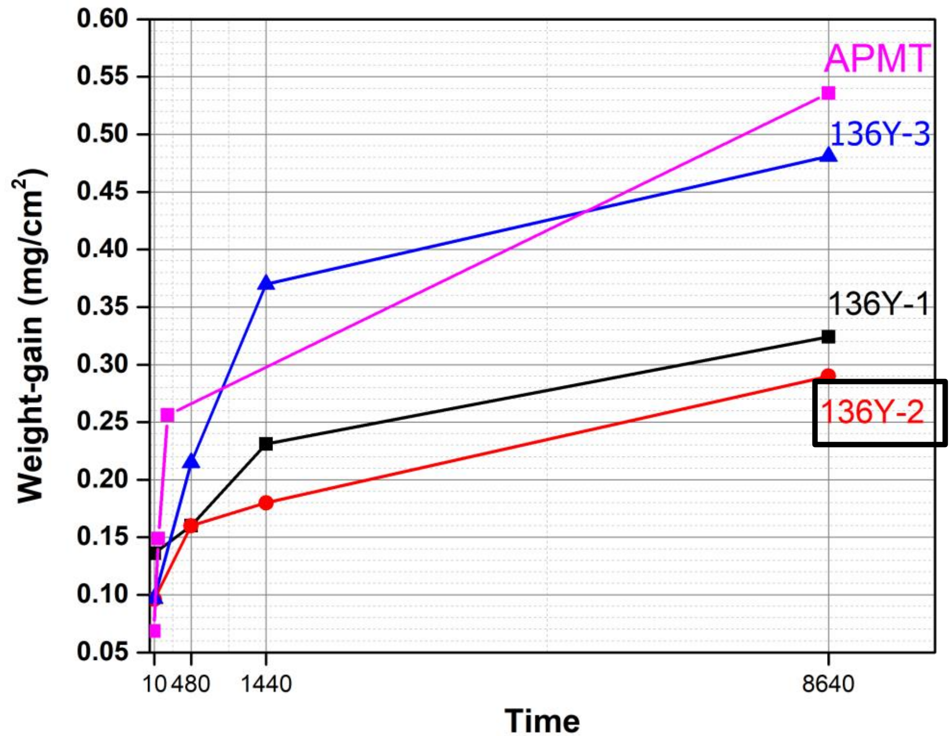
▪ Weight gain result





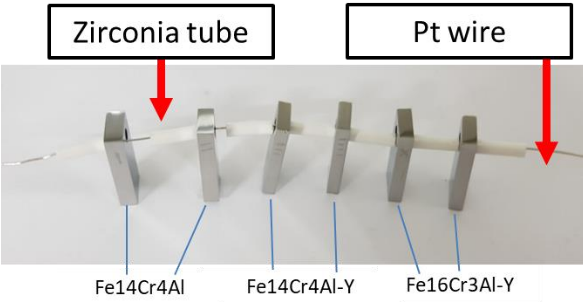
- ✓ The yttrium-doped FeCrAl alloy has excellent high-temperature oxidation resistance.
- ✓ There seems to be an optimum yttrium content in terms of high-temperature oxidation resistance.
- ✓ The weight gain did not increase or decrease linearly with yttrium content.

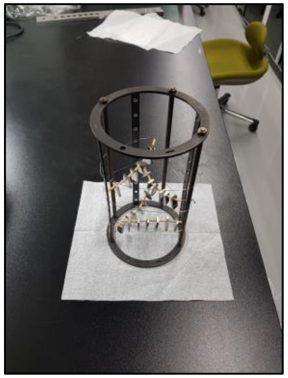
Weight gain values (mg/cm²) of yttrium-doped FeCrAl alloys

Exposure time	Alloy designation		
	136Y-1	136Y-2	136Y-3
10 min	0.136	**0.096**	0.097
3 h	0.160	**0.160**	0.215
8 h	0.231	**0.180**	0.370
24 h	0.324	**0.290**	0.481

Experimental method

- Sample :
  - **144, 144Y-2, 136Y-2**
    10x30x2 mm size.
- Exposure time :
  - 90 days
- Environment :



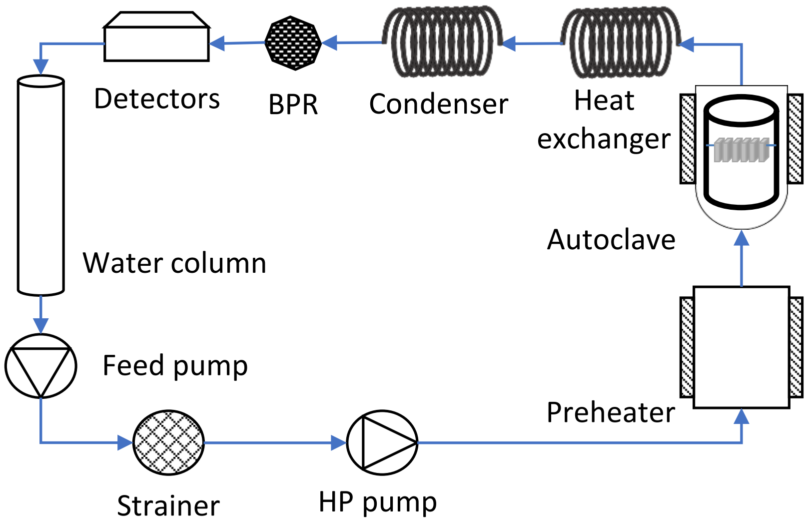


Temperature and pressure conditions of experimental loop

	Primary water	Experimental loop
Temperature	292-325 ℃	360 ℃
Pressure	15.5 MPa	20 MPa

Water chemistry conditions of experimental loop

B (ppm)	Li (ppm)	DO (ppb)	DH (cc/kg)	pH
1000-1200	2	< 10	25	6.8-7.4



Schematic diagram of simulated primary water condition loop

Corrosion test in PWR environment

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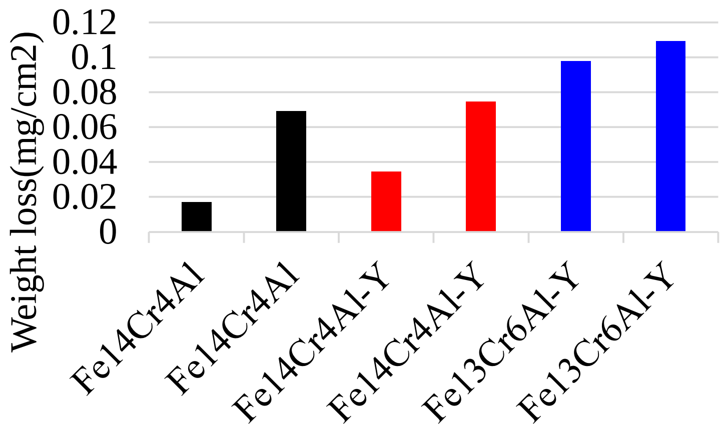
- **Weight gain**
  - ✓ No significant weight difference between specimens, no overall weight change



Weight change of oxidized specimen for 3 months under PWR environment

	Before (g)	After (g)	Weight loss (mg/cm2)	Avg. weight loss (mg/cm2)
Fe14Cr4Al	2.9128	2.9127	0.017241	0.043103
Fe14Cr4Al	5.2702	5.2698	0.068966	
Fe14Cr4Al-Y	4.2448	4.2446	0.034483	0.054598
Fe14Cr4Al-Y	4.1945	4.1940	0.074713	
Fe13Cr6Al-Y	4.4049	4.4043	0.097701	0.103448
Fe13Cr6Al-Y	4.3066	4.3059	0.109195	

Corrosion test in PWR environment

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Microstructure

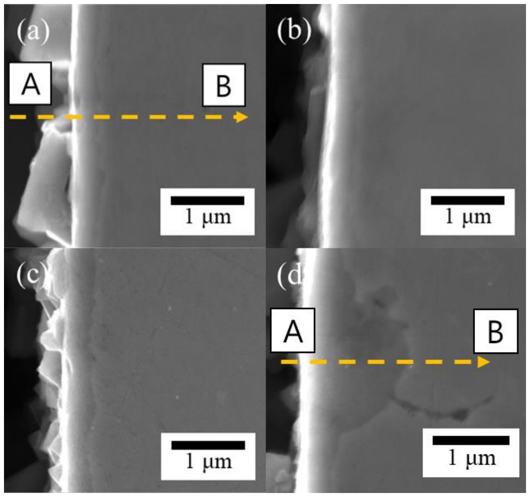


Fig.1 SEM image of (a)Fe14Cr4Al, (b)Fe14Cr4Al-Y, (c) Fe13Cr6Al-Y and (d) Y oxide particle in Fe14Cr4Al-Y

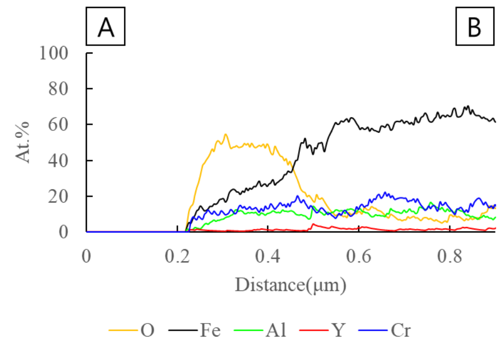


Fig.2 Line-EDS of the oxide scale in Fe14Cr4Al(Fig.1 (a))

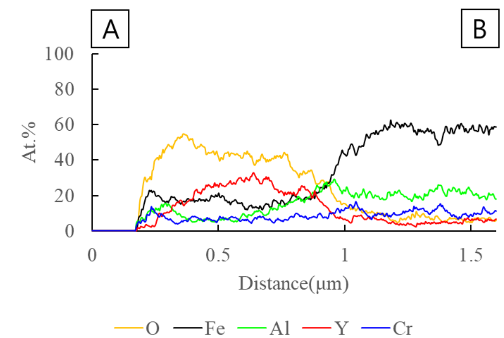


Fig.3 Line-EDS of the oxide scale in Fe14Cr4Al-Y(Fig.1 (d))

SEM analysis

- All specimens have the uniform oxide scale composed of Fe, Cr and Al.
- Y including FeCrAl alloys show Y oxide particles about 1 μm.

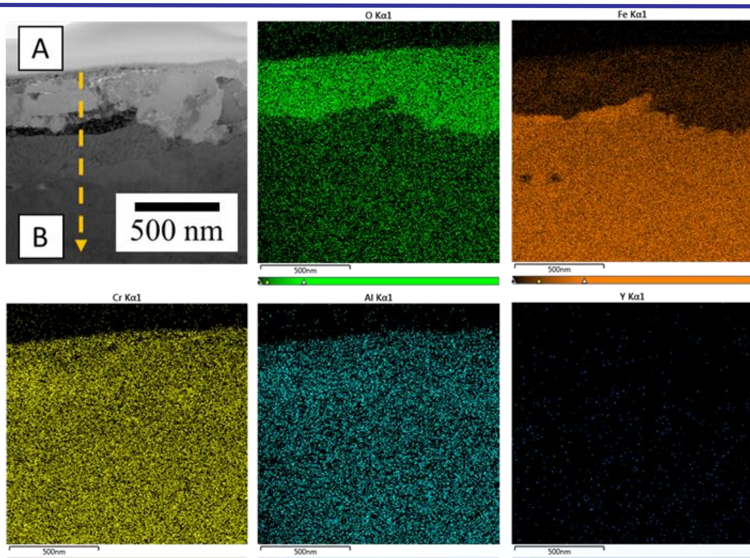
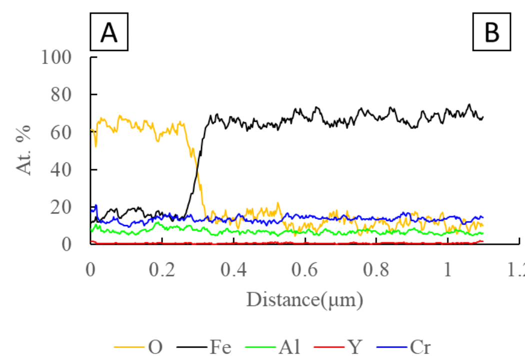


Fig. 4 Map-EDS image of Fe13Cr6Al-Y



	Oxide thickness (nm)
Fe14Cr4Al	402.3121
Fe14Cr4Al-Y	352.7397
Fe13Cr6Al-Y	322.2857

TEM analysis

- ✓ Fe13Cr6Al-Y formed more dense oxide scale.
- ✓ From the FFT result, $FeCr_2O_4$ and Al_2O_3 phase are in oxide scale.
- ✓ The main phase is $FeCr_2O_4$.

Corrosion test in PWR environment

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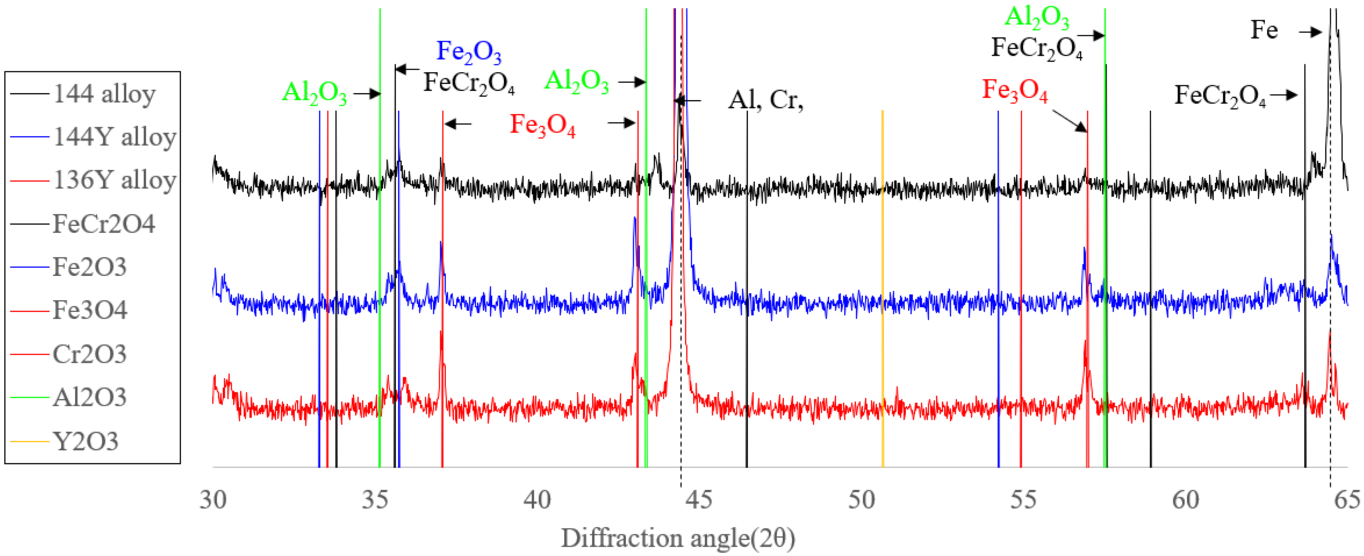
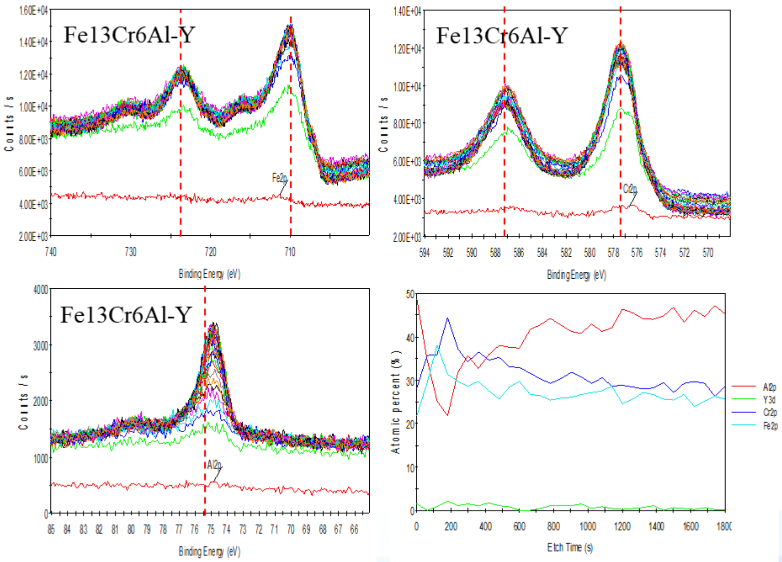
- ## Characteristics of Oxide Scale



- ### XRD analysis
  - $FeCr_2O_4$, Fe_2O_3, Fe_3O_4 and Al_2O_3 peak
  - No Y_2O_3 and Cr_2O_3 peak
  - (because Y_2O_3 has little amount)



- ### XPS analysis
  - ✓ Depth profiling(Sputtering time: 60 sec)

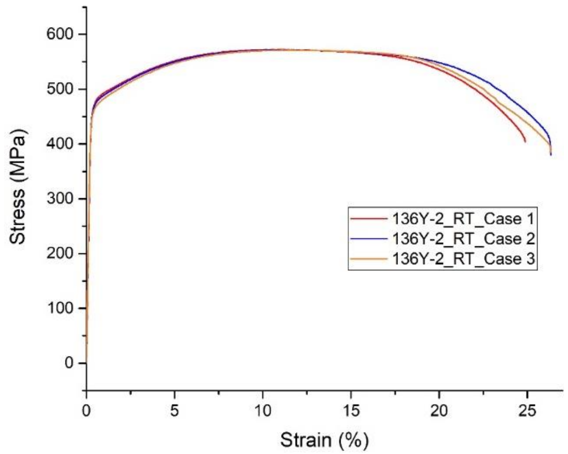
- ### Dominant phase
  - ✓ $FeCr_2O_4$ layer
  - ✓ Fe_2O_3 and Al_2O_3
  - ✓ Top surface: Al →Al_2O_3
  - ✓ Near surface: Fe, Cr →$FeCr_2O_4$
  - ✓ Interface: increasing Al
  - ✓ Fe13Cr6Al-Y: Al concentration is high.(meaning more Al_2O_3)

Mechanical property

- **Tensile test**
  - Sample :
    - **144, 136Y-2**

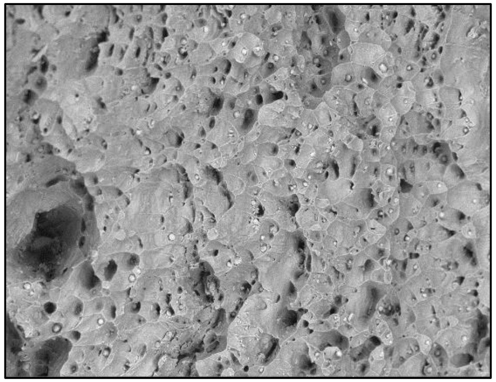
      Plate subsize specimen

      (ASTM E8/E8M-16a)
  - Temperature :
    - Room temperature



Stress-strain curves of 136Y-2 alloy

Alloy designation	Grain size	#	Yield strength (MPa)	Tensile strength (MPa)	Elongation (%)
Zr-Nb-Sn (ring)	-	1	445	768	
144	Elongated grain	1	374.1	519.2	33
136Y-2	41 μm	1	472.6	572.3	24.9
		2	468.6	571.7	26.3
		3	479.2	571.4	26.3



Ductile fracture surface of 136Y-2 alloy

✓ Yield strength of 136Y-2 alloy is similar to Zr-Nb-Sn alloy, but tensile strengths is much lower.

✓ In order to use this alloy for ATF cladding, It is need to improve the more strength.

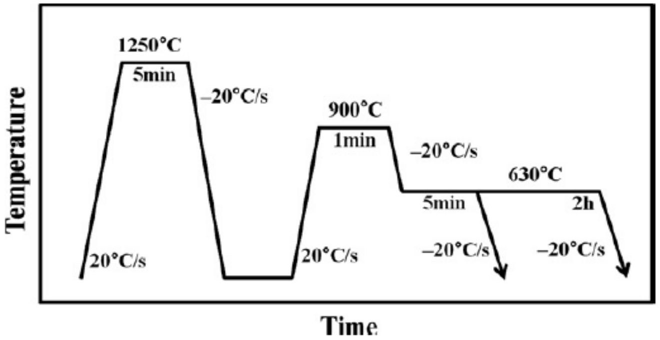
Mechanical property

Nano-sized carbide particle formation

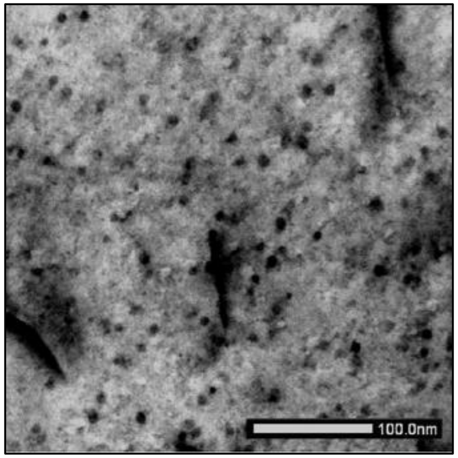
- ✓ Formation of nano-sized (Ti,Mo)C in high-strength low-alloy (HSLA) steels have been studied.
  - Coarsening kinetics of TiC particles can be controlled using molybdenum additions.
  - Mo partly substitutes for Ti in the TiC lattice.

Chemical composition of 0.1Ti-Mo steels (in wt.%)

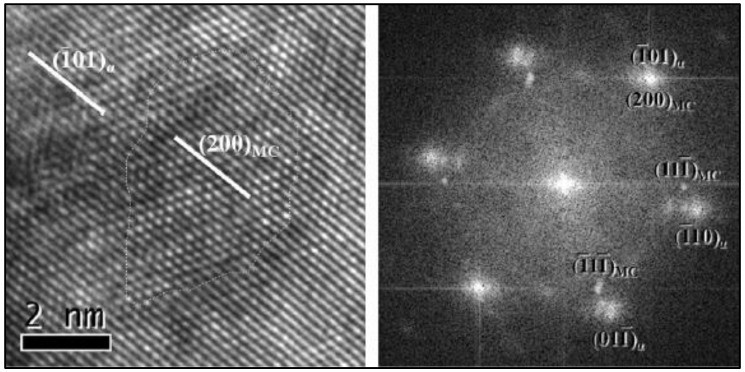
Type	C	Mn	Al	Ti	Mo	W
0.1 Ti-Mo	0.039	1.99	0.022	0.084	0.20	-



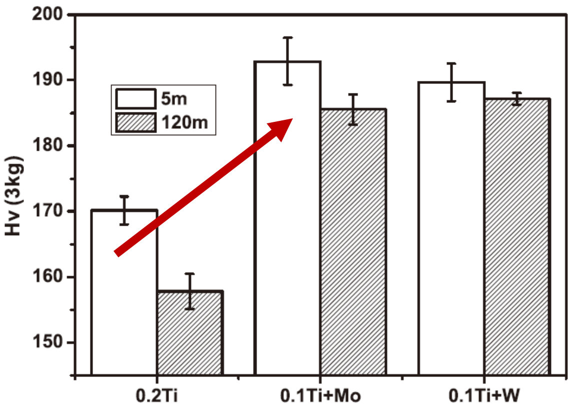
Schematic diagram showing the two-step heat treatment.



STEM bright field images for 0.1Ti–Mo



HRTEM image of a 0.1Ti–Mo sample and its fast Fourier transform image



Vickers hardness results

Jang, Jae Hoon, et al. "Stability of (Ti, M) C (M= Nb, V, Mo and W) carbide in steels using first-principles calculations." Acta Materialia 60.1 (2012): 208-217.

Summary

부산대학교 Materials in Nuclear Systems Lab.

✓ Yttrium effect in high temperature oxidation

- In the as-received yttrium-doped FeCrAl alloys, yttrium-rich intermetallic particles as YFe_4Al_8 were distributed uniformly in the matrix, which has not been reported before.
- The oxide adherence enhancement by the addition of yttrium
  - Mainly due to the change of the oxide growth mechanism by yttrium segregation at the grain boundary of the aluminum oxide, rather than the mechanical "keying effect" caused by $Y_3Al_5O_{12}$ pegs.

✓ Corrosion test in PWR environment

- After 3month test in PWR environment, there is no significant weight difference between specimens and no overall weight change.
- Top surface: Al_2O_3, Near surface: $FeCr_2O_4$
- More dense and thin oxide layer formed on 136Y alloy than other alloys.

✓ Mechanical property

- The mechanical property of Y doped alloys is not enough for ATF cladding.
- The FeCrAl alloys with improved strength are being fabricated and evaluated.