한국원자력학회
2021 추계학술발표회

The effect of annealing temperature of $NiFe_2O_4$ thin film prepared by E-beam evaporation method for simulated specimen in PWR system

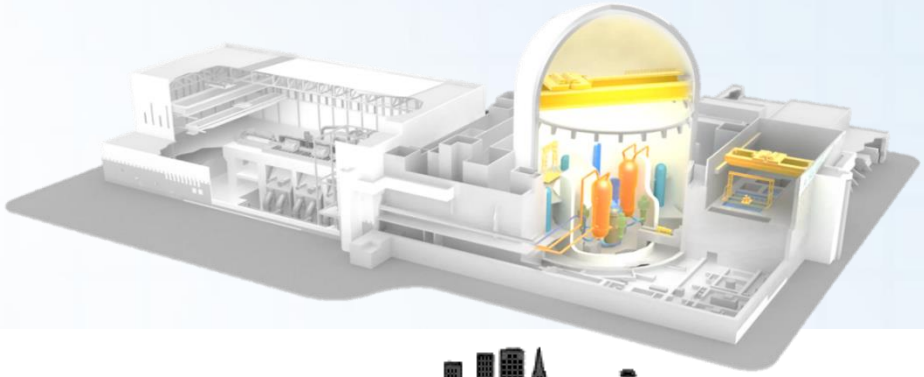
KOREAN
NUCLEAR
SOCIETY
2021 AUTUMN MEETING

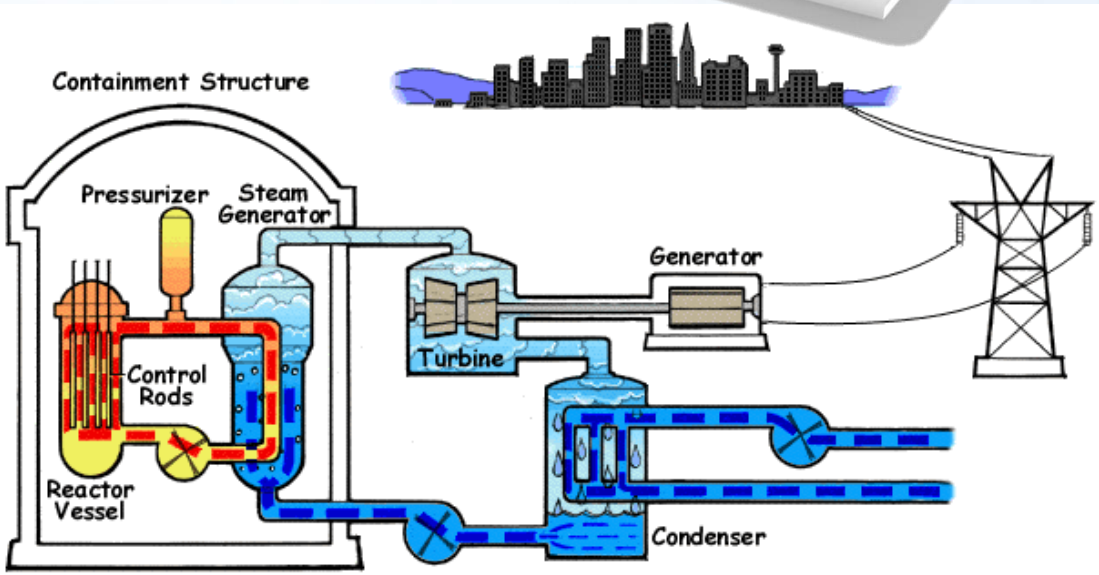
Decontamination process

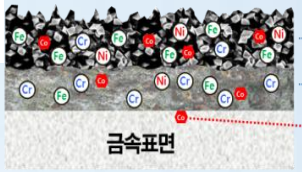
Chemical decontamination for primary coolant system for NPP

(프랑스 AREVA HP/CORD 기술 대비 폐기물 발생량 30% 저감)

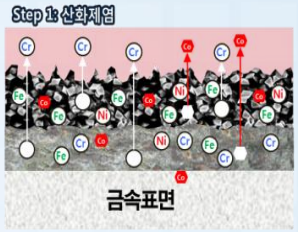
- Inventive chelating reagent-free chemical decontamination agents
- Reduction of worker's dose exposure and safety intensification
- Minimization of secondary waste solution and increased safety disposal







Multi-step HYBRID 제염공정



(산화제염) Cr 주성분의 부식산화막 용해

$Cr_2O_3 + 2MnO_4^- + H_2O \rightarrow 2HCrO_4^- + 2MnO_2$

산화제 파괴

$4KMnO_4 + 5N_2H_4 + 12H^+ \rightarrow 4K^+ + 4Mn^{2+} + 5N_2 + 16H_2O$

(환원제염) Fe & Ni 주성분의 부식산화막 용해

(Cu⁺ regeneration) $N_2H_5^+ + 4Cu^{2+} \rightarrow N_2 + 5H^+ + 4Cu^+$

$Ni_xFe_{3-x}O_4 + 8H^+ + 2Cu^+ \rightarrow (3-x)Fe^{2+} + xNi^{2+} + 2Cu^{2+} + 4H_2O$

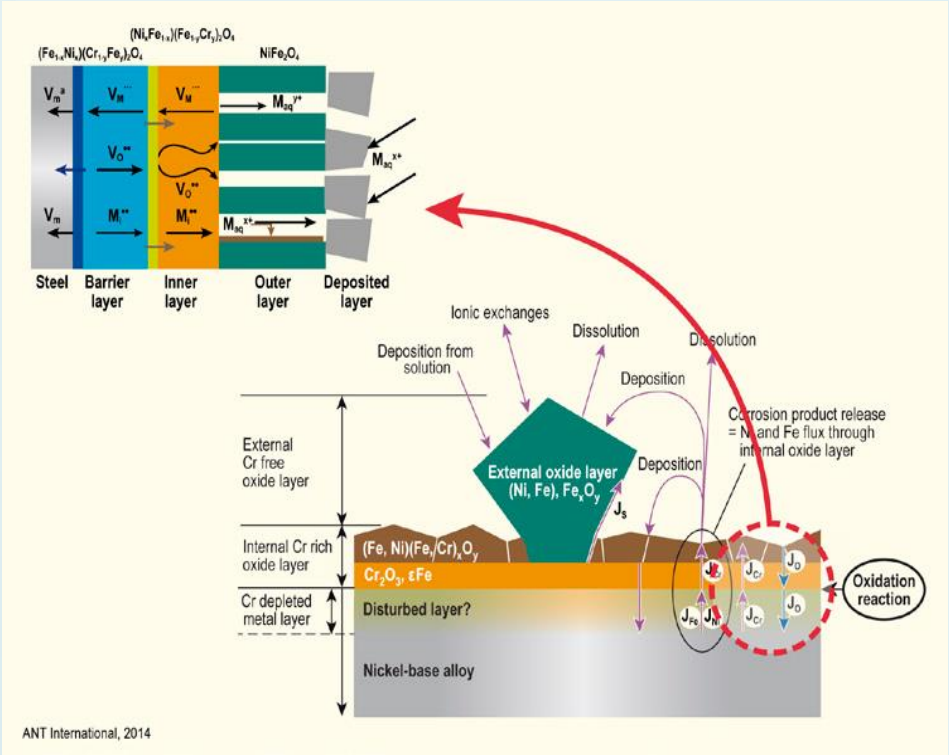
환원제 파괴

$2H_2O_2 + N_2H_4 \Rightarrow N_2 + 4H_2O$

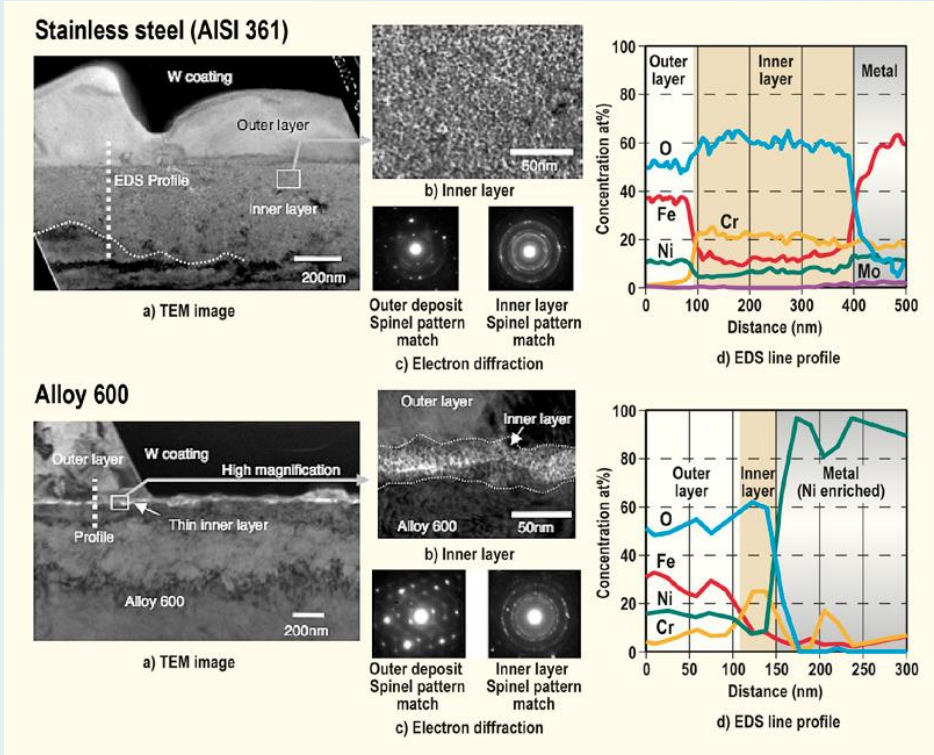
Corrosion oxide layer in PWR

The characterization of oxide layer in PWR

Oxide layer in PWR system (SS or Ni-Fe based alloy)



Oxide layer on SS and alloy 600 substrate



- Inner oxide layer
  (Cr_2O_3 or chromium rich spinel oxide)
- Outer oxide layer
  (spinel type nickel ferrite, chromium free (<5% Cr))

- TEM cross-section image of the oxide film on AISI 361 SS and alloy 600 under simulated PWR operating coolant conditions at 320 ℃ for 380 and 1730 hours, respectively.

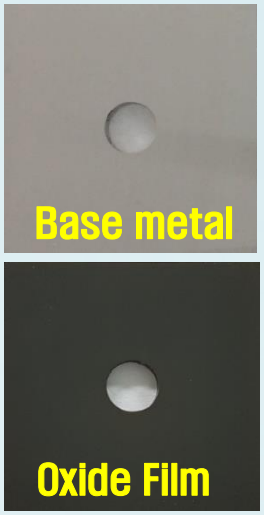
Suat Odar, CRUD in PWR/VVER coolant, V2

How to prepare oxide layer ?

Autoclave & E-beam evaporator

Autoclave system

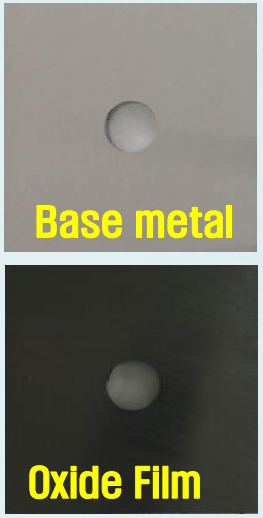
H_2O
Na_2H_4·EDTA
N_2H_4
B, Li
DO



- Simulated condition of PWR
- $FeCr_2O_4$ oxide layer
- Thickness control
- Multi-step and no uniformity

E-beam evaporator system

$NiFe_2O_4$
target

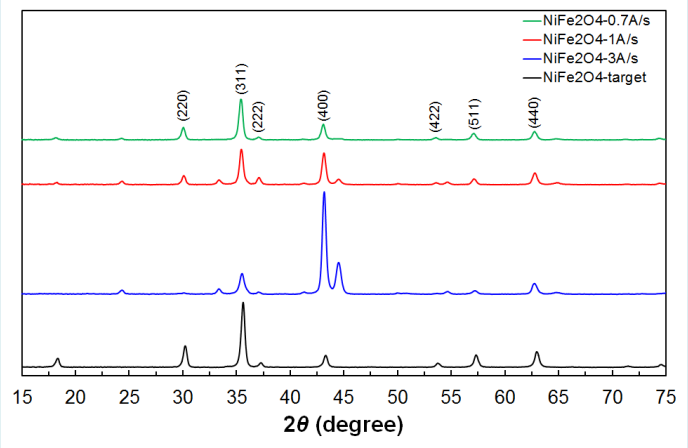


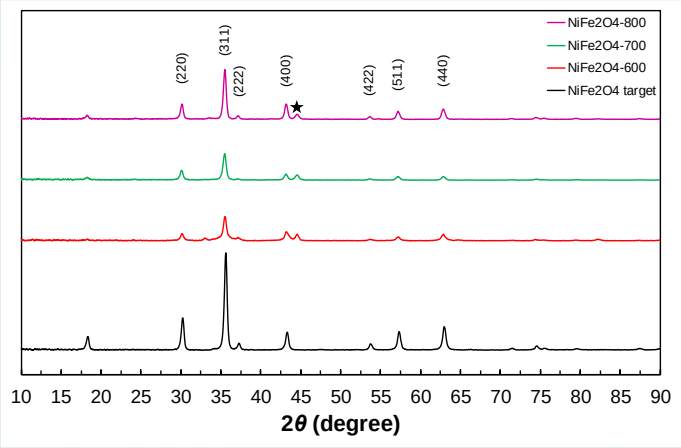
- Precise thickness control
- Fast deposition (0.7 Å/s)
- Low roughness
- Simple process
- Requirement for crystallization

XRD and SEM analysis

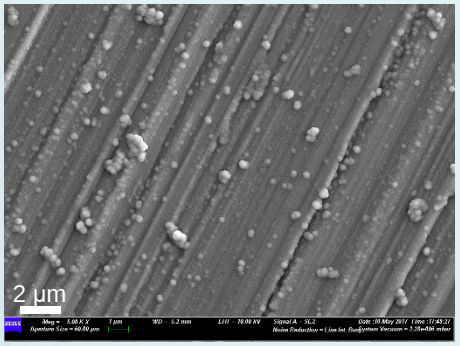
XRD pattern and surface morphologies

E-beam evaporator system

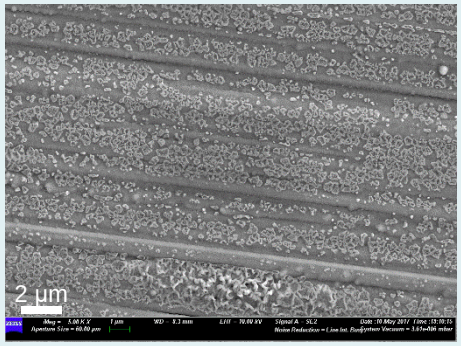




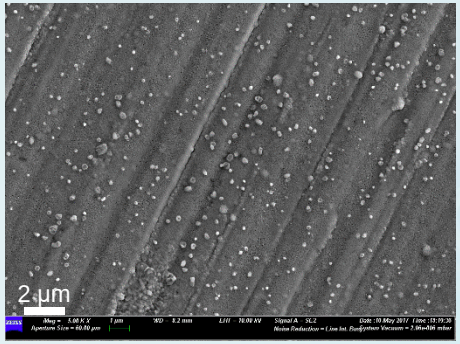
< XRD patterns of $NiFe_2O_4$ according to deposition condition >



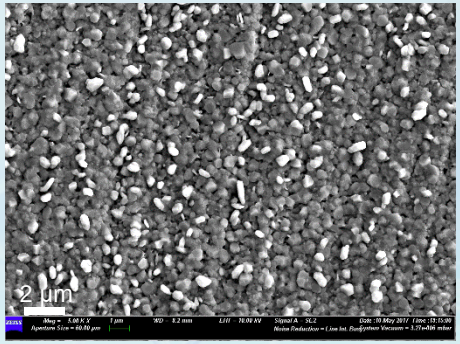
600 ℃, 1h



700 ℃, 1h



700 ℃, 10h



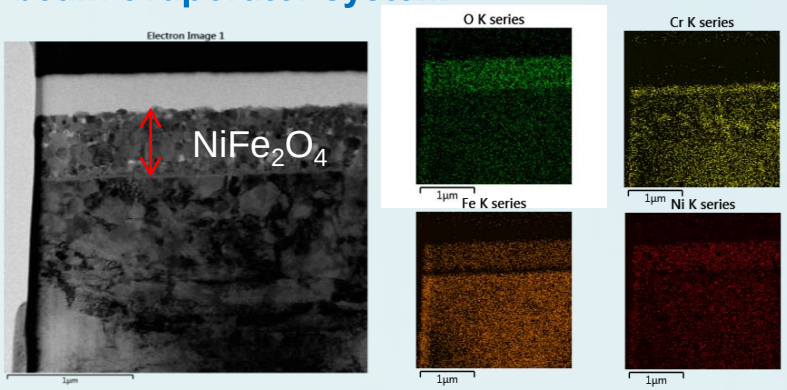
800 ℃, 1h

< SEM images of $NiFe_2O_4$ according to heating condition >

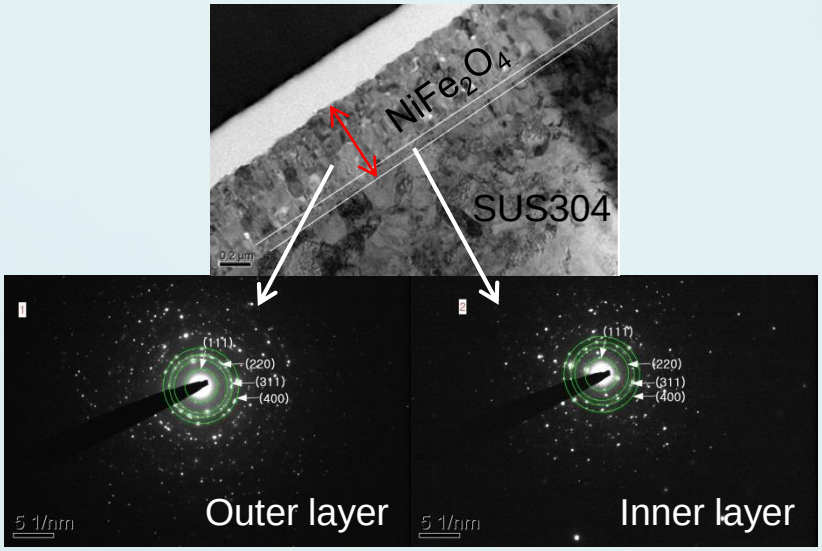
TEM and XPS analysis

EDS mapping, SAED pattern, XPS depth profile

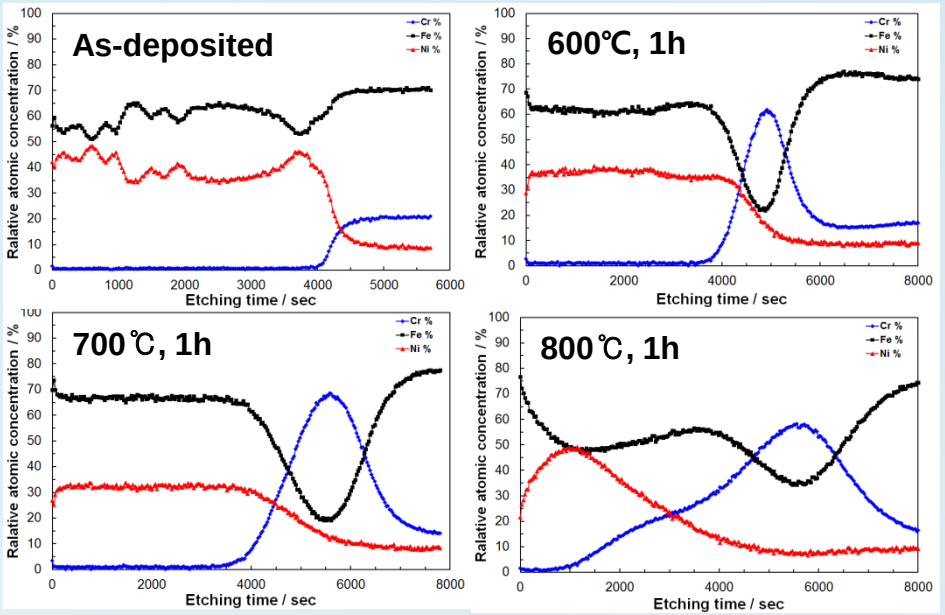
E-beam evaporator system



< EDS mapping of $NiFe_2O_4$ >



<Cross-section image and SAED pattern of $NiFe_2O_4$>

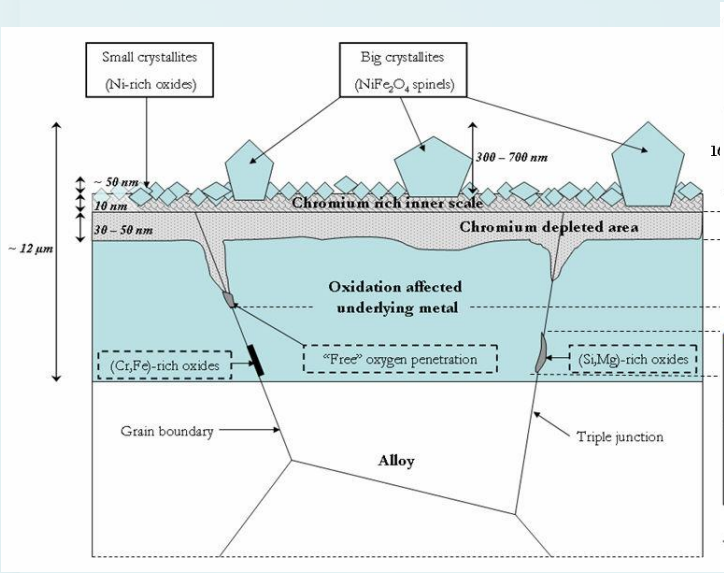


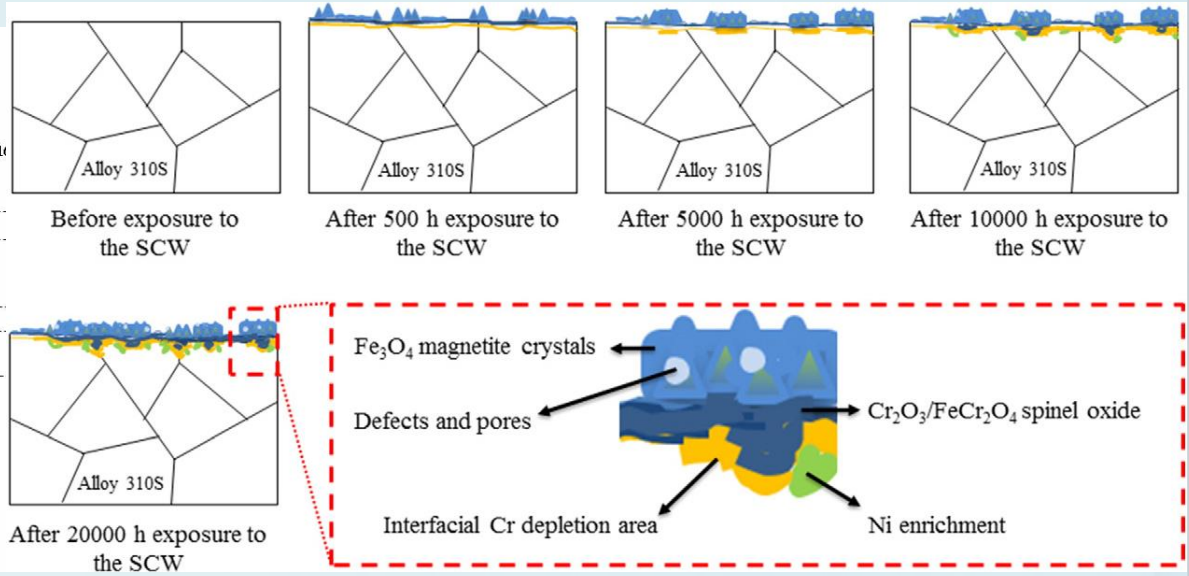
< XPS depth profiles of $NiFe_2O_4$ >

- **$NiFe_2O_4$ oxide layer was optimized and well defined by XRD and TEM image.**
- **Inner and outer oxide layer were formed by heat treatment(XPS).**
- **The thickness of oxide layer was precisely and uniformly controlled by E-beam system.**

Oxide layer growth mechanism

Oxide film structure Ni-Fe-Cr on SUS



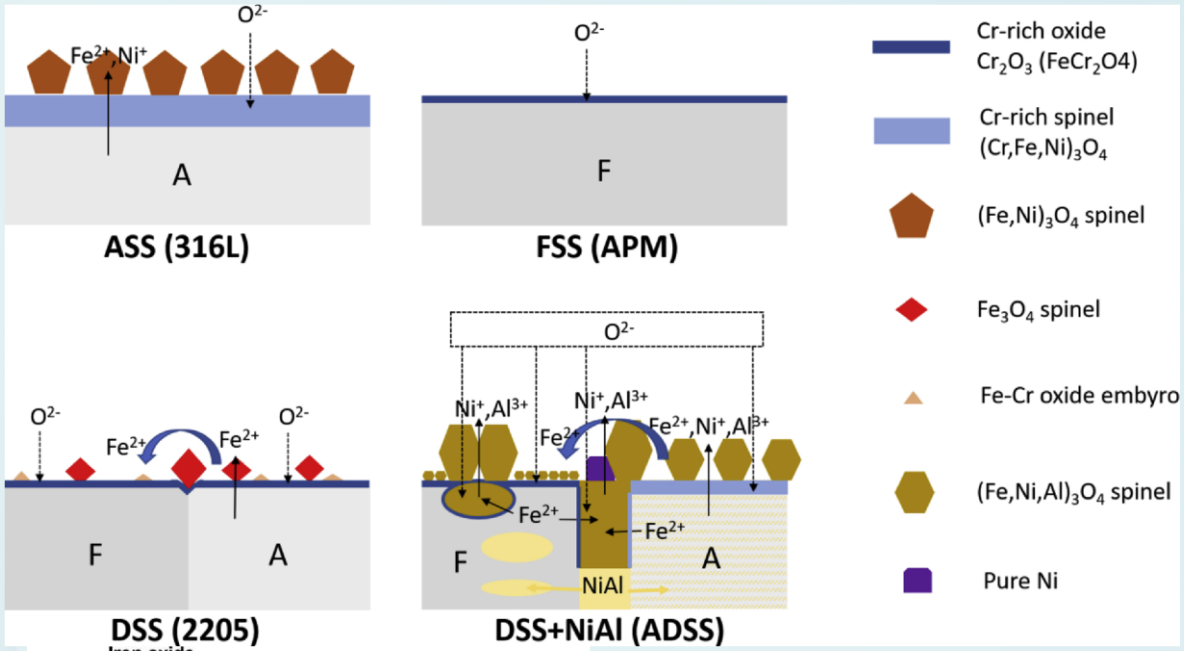


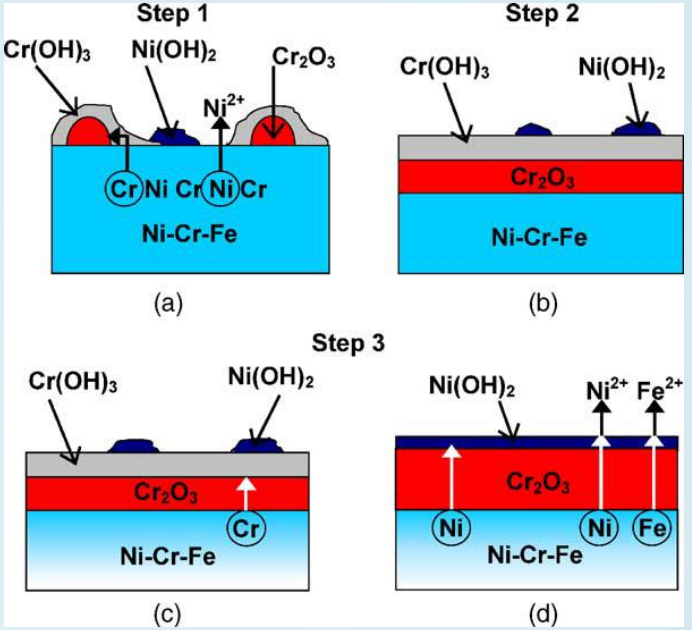
B. Ovanessian, et. al, Materials Science Forum, 595, 2008
Y. Behnamian, et. al, Materials Characterization, 120, 2016

- **Outer oxide layer was composed of large crystallites ($NiFe_2O_4$ spinel oxides) and smaller grains of a mixed oxide of nickel, chromium and iron with thickness of 100 nm.**
- **Compact and continuous inner layer of Cr rich spinel/Cr_2O_3 oxide was identified at the metal-oxide interface.**
- **The composition of oxide layer may form on the surface of stainless steel depending on the (1) oxygen concentration, (2) temperature, (3) substrate, and etc.**

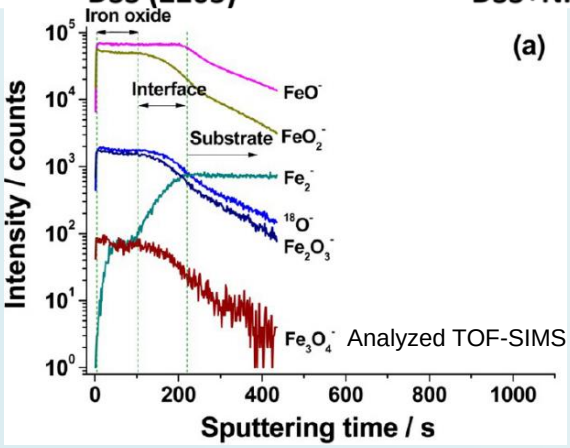
Future work

Oxide film for decontamination application





Q. Xiao. Et al, Corrosion Science 177, 2020
A. Machet, et. al, Electrochimica Acta, 49, 2004



(a) Analyzed TOF-SIMS

- **Preparation of μm scale oxide film.**
- **Characterization of metal oxide layer in depth.**
- **Investigation of composition of inner layer according to the substrate (ex;SUS, Inconel, and Carbon steel).**
- **Decontamination test with simulated oxide specimen.**

Summary

Oxide film structure Ni-Fe-Cr on SUS

- Simulated corrosion oxide layer(and $NiFe_2O_4$) was prepared by autoclave and E-beam system for the chemical decontamination test.
- The oxide layer was characterized by SEM, TEM, XRD and XPS.
- Duplex structure(inner and outer layer) was observed in simulated specimen.
- E-beam system provided deposition of nickel ferrite(500 nm) with high crystallinity (XRD).
- The composition of oxide layer may form on the surface of stainless steel depending on the temperature.


감사합니다