Corrosion Behavior of Anodized and Cathodic Plasma Electrolyte Oxidation (CPEO) coating on stainless steel used in nuclear spent fuel dry storage canister

Jun Heo, Jae Woo Lee, and Sung Oh Cho *

NQe Nuclear & Quantum Engineering

Department of Nuclear & Quantum Engineering, Korea Advanced Institute of Science and Technology

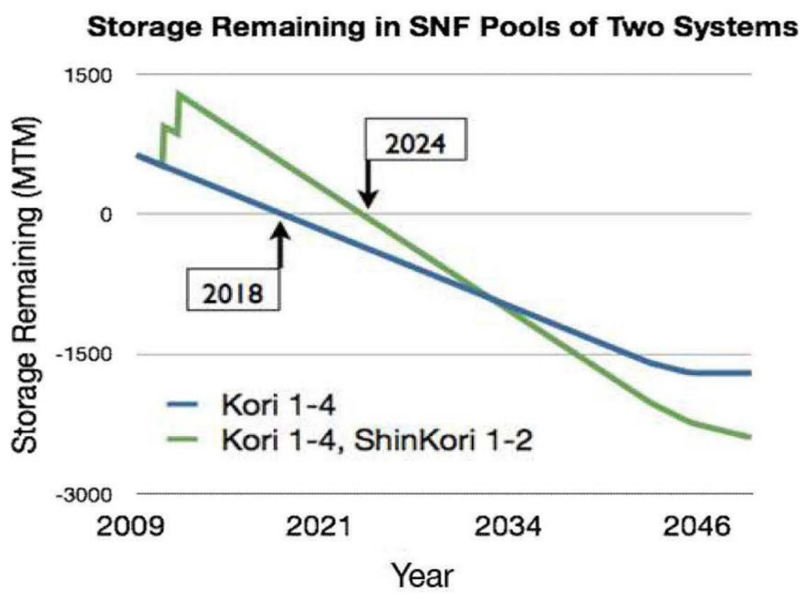
KAIST

*e-mail: socho@kaist.ac.kr

Introduction

Spent Nuclear Fuel (SNF) dry storage system

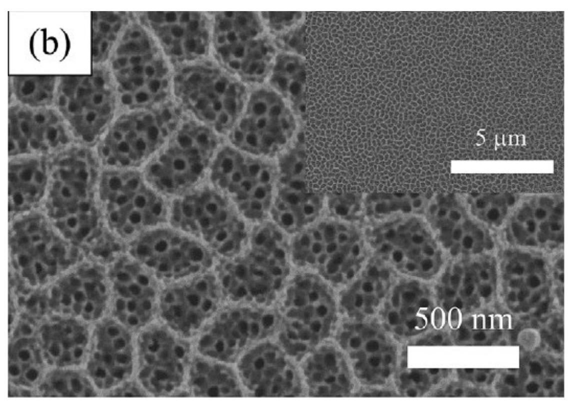
- ❖ Nuclear spent fuel storage (Wet vs. Dry) is one of the most significant issue spotlighted.
- ❖ Wet storage system (commonly used) is approaching saturation state → about 2024 with Kori
- ❖ Need of dry storage system with metal (**stainless steel**) canister



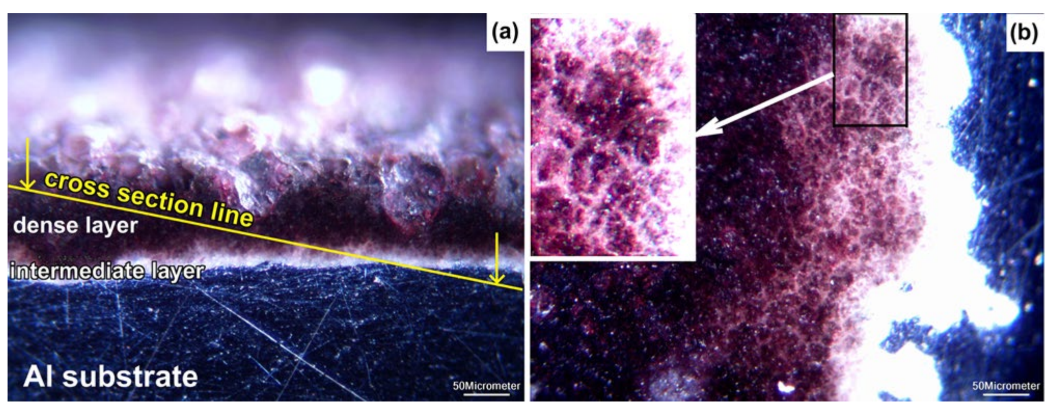
- ❖ Metals suffer **various corrosion issues** under harsh environments

Metal durability developing technologies

- ❖ **Cathodic Plasma Electrolyte Oxidation (CPEO)** coating technology is in the limelight to be applicated on stainless steel for corrosion protection
- ❖ **Anodization** has the similar concept with CPEO of applying voltage to the metal in a certain electrolyte, surface morphology change in both ways



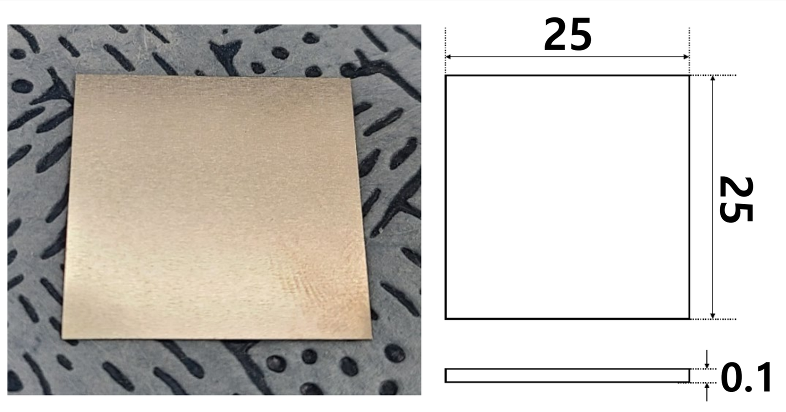
→ Anodization of stainless steel



→ Plasma electrolytic oxidation of aluminum alloy

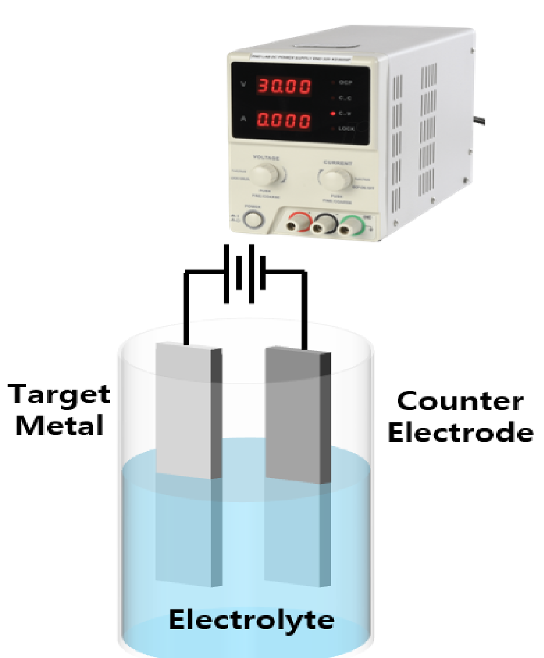
Experimental

Sample Preparation



- ❖ Samples were sonicated in acetone, ethanol, and deionized water (5 min. each)
- ❖ Dried in vacuum oven of 60 ℃

Anodization & Cathodic Plasma Electrolyte Oxidation (CPEO)

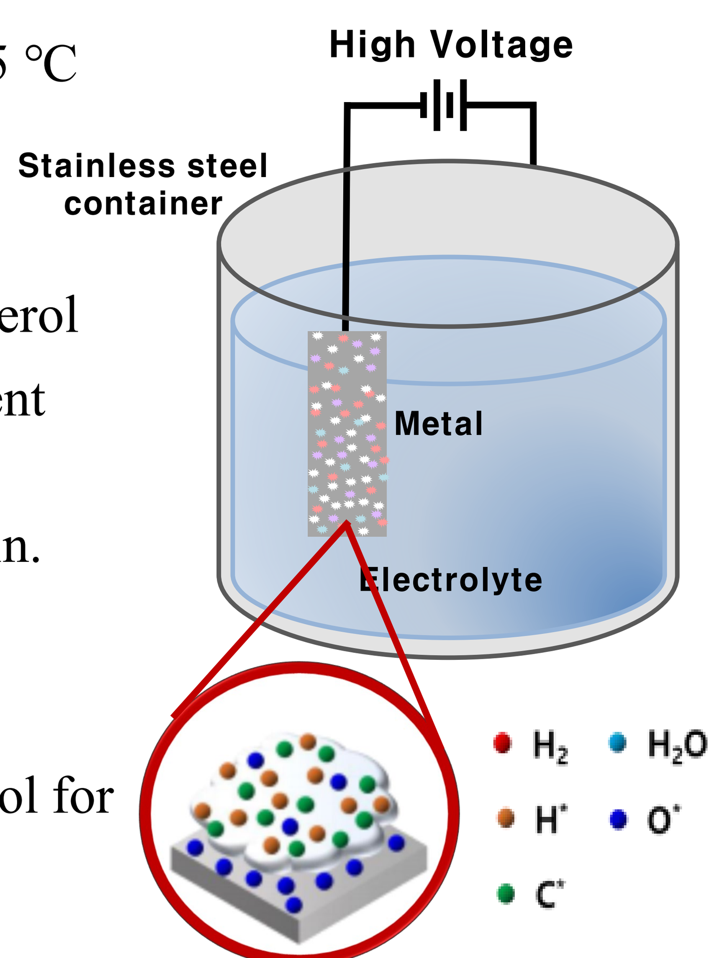


Anodizing condition

- ❖ Cooling bath was used at temperature of 25 ℃
- ❖ Target metal: 304 SS
- ❖ Counter electrode: Platinum sheet
- ❖ Electrolyte: 0.1 M H_2O + 0.1 M NH_4F in E.G
- ❖ Applied voltage: 60 V
- ❖ Duration: 7 min.
- ❖ After anodization, specimen immersion in ethanol for 10 min. & kept in vacuum oven at 50 ℃

CPEO condition

- ❖ Cooling bath was used at temperature of 25 ℃
- ❖ Working electrode: 304 SS container
- ❖ Counter electrode: 304 SS
- ❖ Electrolyte: 10 wt.% borax + 15 wt.% glycerol
- ❖ Potential: -180 V with unipolar direct current (above breakdown potential of SS, -110 V)
- ❖ Initial increase rate: 1 V/s & kept for 10 min.
- ❖ Frequency: 100 Hz
- ❖ Duty cycle: 45% for negative potential
- ❖ After CPEO, specimen immersion in ethanol for 10 min. & kept in vacuum oven at 50 ℃

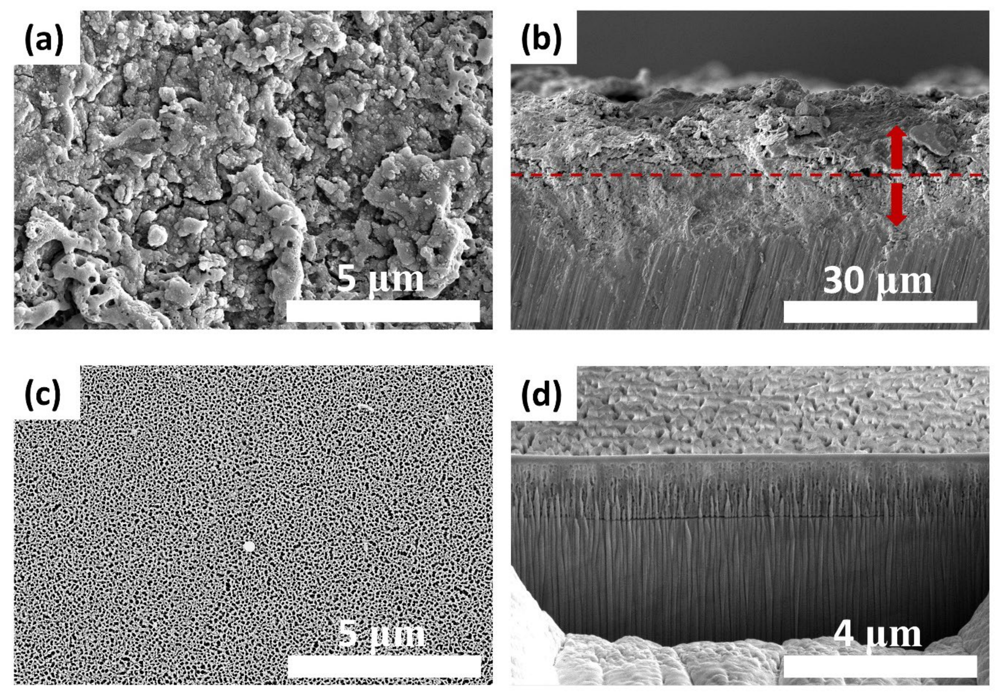


Electrochemical test cell conditions

- ❖ Working electrode: Surface treated 304 SS (surface ~ 0.2 cm²)
- ❖ Counter Electrode: Platinum wire
- ❖ Reference electrode: Saturated calomel electrode
- ❖ Potential range: ± 600 mV
- ❖ Electrolyte: Artificial seawater
- ❖ OCP (open circuit potential) was preconditioned for 1200 sec.

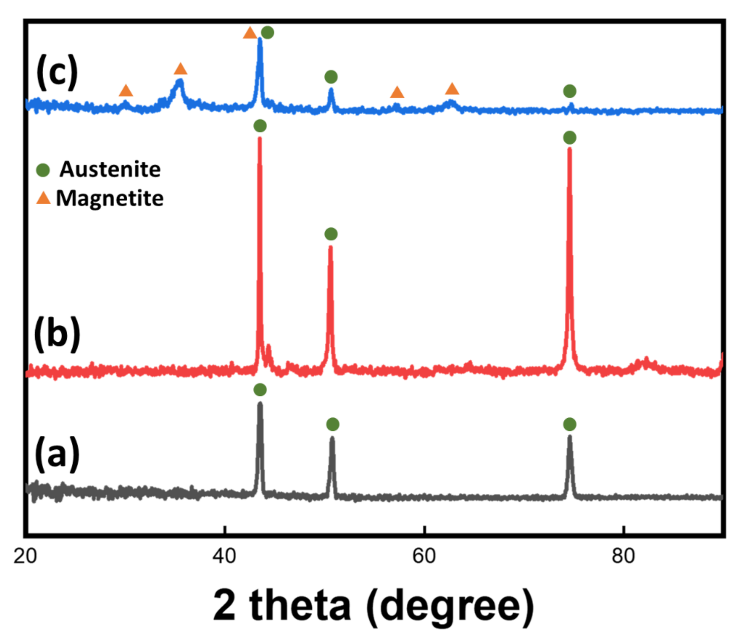
Results & Analysis

Surface morphologies analysis of CPEO coated and anodized samples

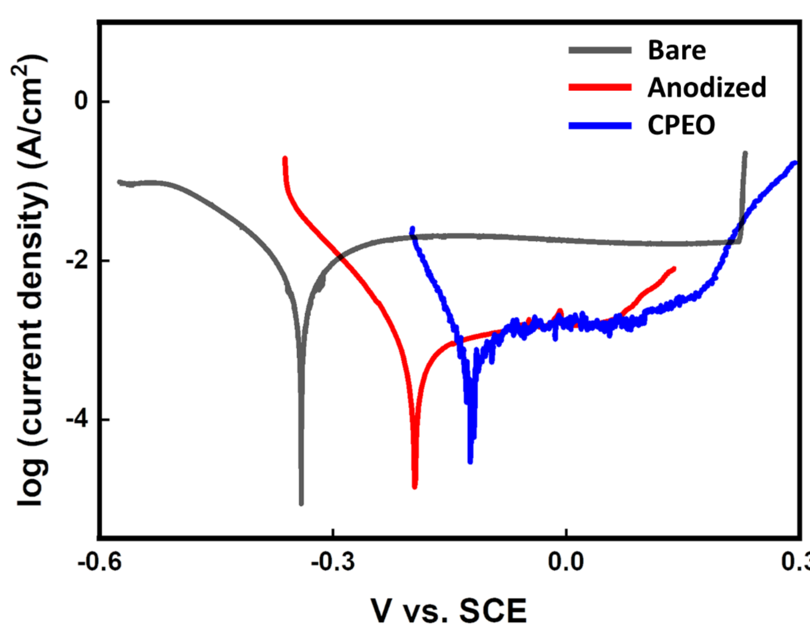


- ❖ Surface of the CPEO coated sample (a) is rough with fine particles / pores / cracks
- ❖ Pores / cracks zone experienced high energy of the plasma discharge
- ❖ Cross sectional view of CPEO (b) depicts no cracks / pores reaching the substrate
- ❖ In CPEO, oxide layer grows both inward and outward (total thickness: **22.3 um**)
- ❖ Uniform bonding of inner dense layer provides high adhesive strength
- ❖ For Anodization, stable and uniform oxide layer was fabricated (c, d)
- ❖ Oxidation and dissolution (etching) reaction fabricated uniform nanopores (c)
- ❖ Average pore diameter ~ **52 nm** / Thickness of oxide layer ~ **1.14 um**

- ❖ Bare 304 SS (a): Austenite
- ❖ Anodized 304 SS (b): Austenite (due to amorphous structure of oxide layer)
- ❖ CPEO coated 304 SS (c): Austenite + Magnetite → Chemically stable oxide layer



Electrochemical measurements



Type	E_{corr} (mV/SCE)	i_{corr} (A/cm²)	CR (mm/yr)
Bare SS	-319.2	1.83×10^{-6}	1.973×10^{-2}
Anodized	**-222.0**	5.68×10^{-7}	**6.124×10^{-3}**
CPEO	**-125.5**	6.57×10^{-7}	**7.084×10^{-3}**

- ➢ E_{corr} : Anodized < CPEO
- ➢ **Corrosion Rate (CR)**: Anodized < CPEO

- ➢ Less chance of corrosion attack with **CPEO** (stable Fe_3O_4 layer)
- ➢ Similar CR, but **anodized** sample showed better CR status

Conclusion

- ➢ CPEO: 22.3 um oxide layer (in / outward) with cracks & pores due to plasma discharge
- ➢ Anodization: nanoporous structure with 1.14 um constant thickness oxide layer
- ➢ With CPEO, chance of corrosion (E_{corr}) was lower and adhesion of oxide layer was advantageous, but CR was higher due to cracks or pores
- ➢ With Anodization, adhesion of oxide layer was inferior and corrosion probability was higher, but CR was lower due to uniform nanoporous oxide layer

References

▶ Braun _ Considerations regarding ROK spent nuclear fuel management options, Nuclear Engr. And Tech. 45.4(2013)
▶ Sourav Kr. Saha _ Self-organized honeycomb-like nanoporous oxide layer for corrosion protection of type 304 stainless steel in an artificial seawater medium, Journal of Molecular Liquids 296(2019)
▶ Aleksey B. Rogov _ The Role of Cathodic Current in Plasma Electrolytic Oxidation of Aluminum: Phenomenological Concepts of the "Soft Sparkling" Mode, Langmuir 33(2017)