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The effect of pH adjuster type on general corrosion characteristics of Alloy690TT in pressurized water reactor

Hui-won Kim[1,2], Seong-Jun Ha[1], Il Shon [2], Hee-Sang Shim[1,*]

[1]Korea Atomic Energy Research Institute(KAERI)
[2]DMSE, Yonsei University

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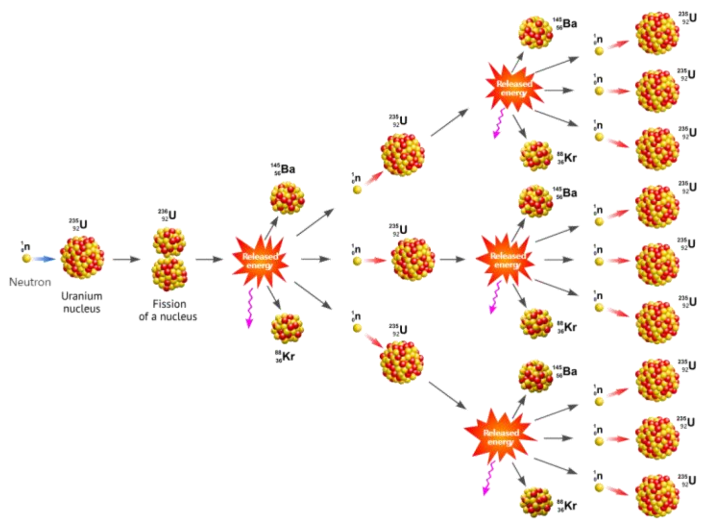
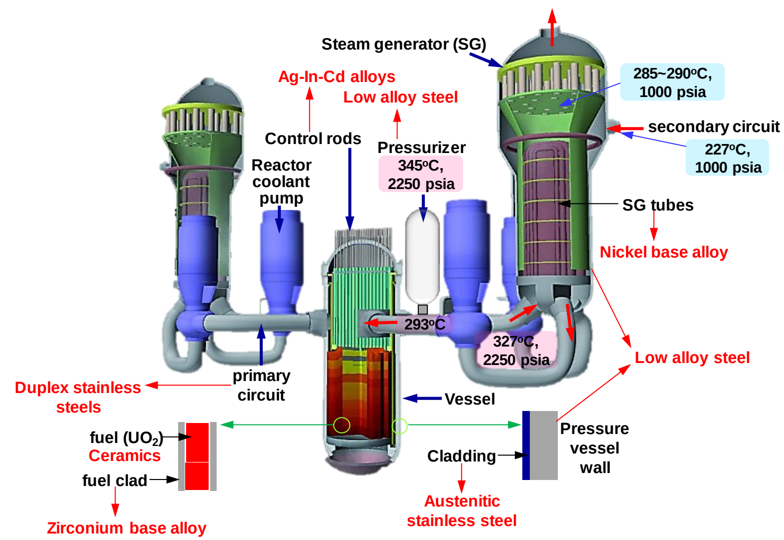
Contents

Research background (1 / 4)

Usage of B and Li in primary coolant of pressurized water reactors





- ^{10}**B is used to control of core reactivity**, continuous fission reaction.
- B concentration in primary water (→**Acidic environment**)

  1,100~1,600 ppm(BOC) / 10~50 ppm(EOC)
- Alkali agent addition to control the pH for corrosion

  ^{7}**LiOH** is used to control the pH of coolant
- ^{10}B : 19.8% : reactivity control **(σa : 4,010 barn)**

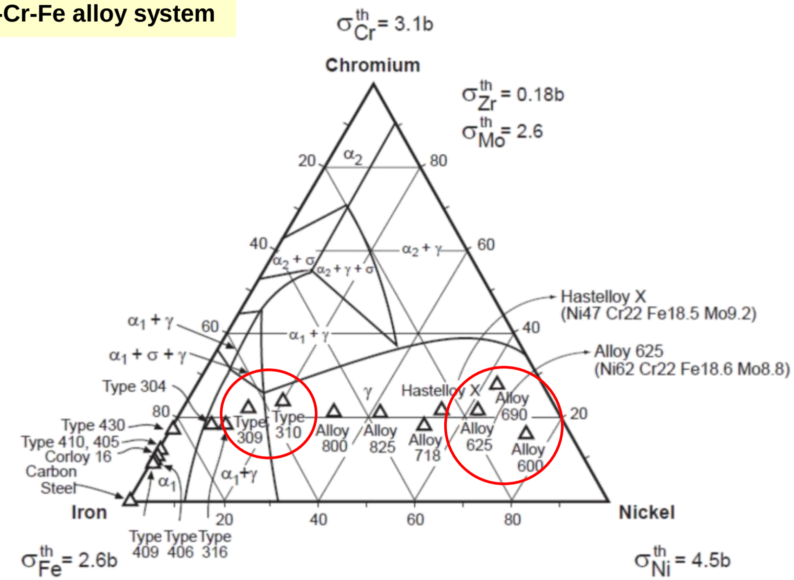
  $^{10}B + n_{thermal} \rightarrow {}^{7}Li + {}^{4}He + 2.35\ MeV$

- **Nuclear power plant materials**
  - Low alloy steels :~1,900 t
  - Stainless steels : ~ 900 t
  - Nickel base alloys : ~280 t
  - Others : Zr-base alloys, nuclear materials (Ag-In-Cd), Ceramics, Cu, Ti alloys, etc
- **Primary surface exposure** :
  - Nickel base alloys : ~ 70%
  - Zr base alloys : ~ 20%
  - Stainless steel and others : ~10%

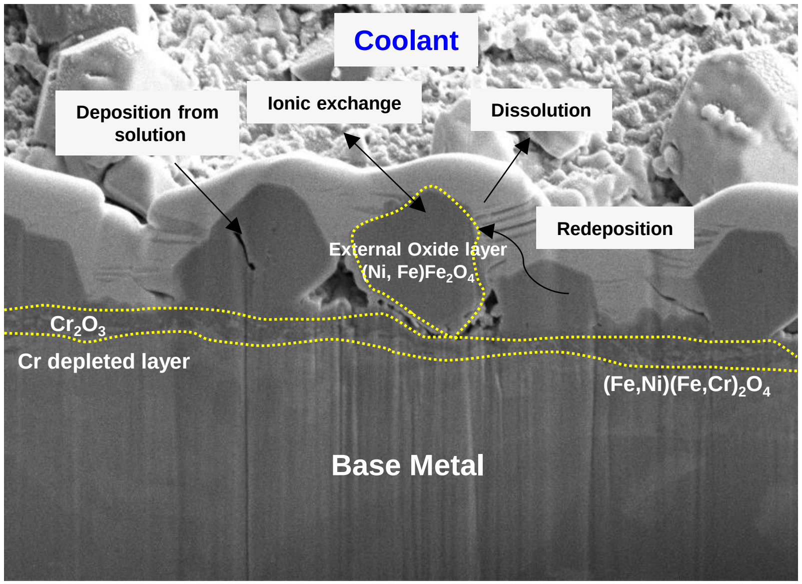
Research background (2 / 4)

Oxidation mechanism of nickel-base alloys and stainless steels

Ni-Cr-Fe alloy system



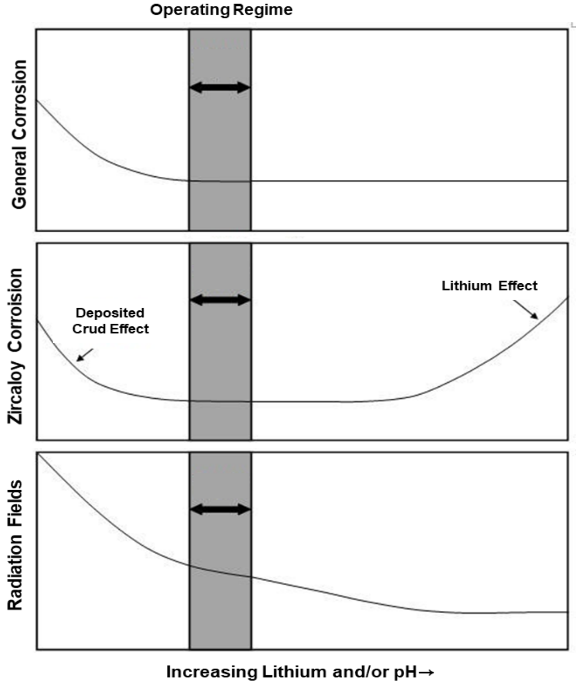
Corrosion release

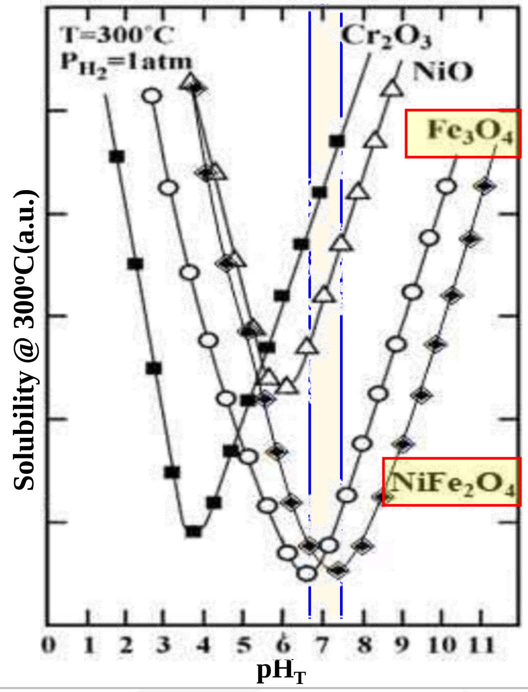


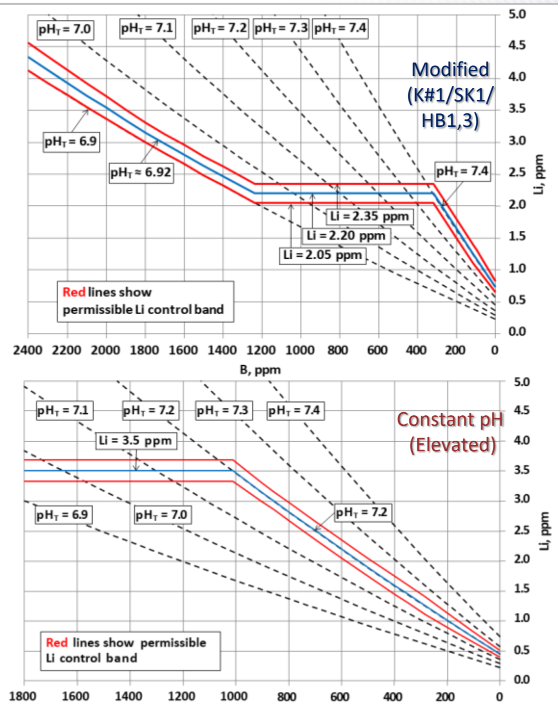
- **Ni-base alloys** and **stainless steels** are in **Ni-Cr-Fe alloy** system→ **Similar corrosion behaviors**
- **Double layered oxide** : (Internal oxide) Cr-rich oxide, (External oxide) Fe-Ni-rich oxide due to high diffusivity of Fe and Ni through passivation layer comparing to that of Cr

Research background (3 / 4)

pH management in primary coolant of PWRs





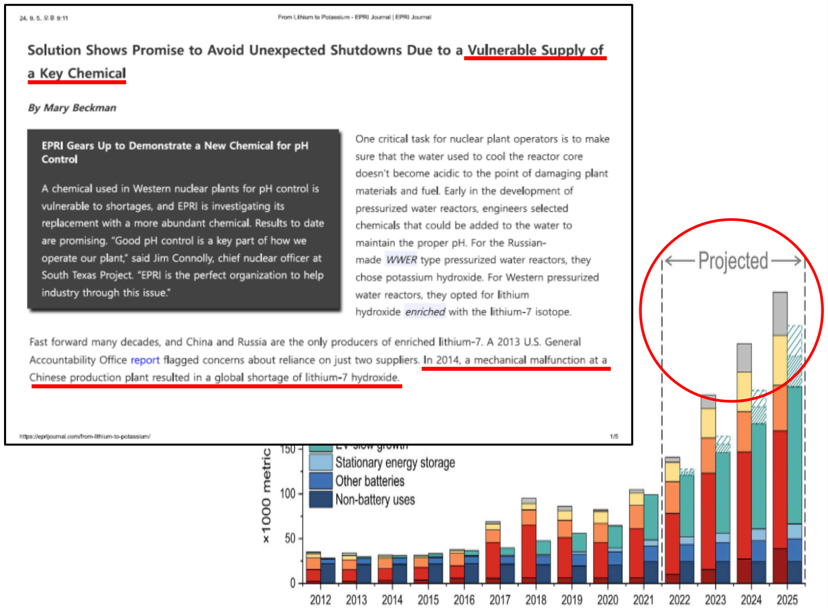


- **Chemistry optimization :** To minimize **1) corrosion of consisting materials, 2) fuel corrosion and crud deposit, 3) radiation buildup**
- Importance of major oxide solubility: 1) **Nickel ferrite($NiFe_2O_4$),** 2) **Magnetite(Fe_3O_4)**, background for **pH_T 6.9-7.4**
- pH management program 1) **Modified elevated chemistry** 2) **Constant chemistry** applied into domestic NPP

Research background (4 / 4)

Demand and research in alternative of ^7LiOH; KOH

- Lithium supply shortage and its consumption trend


24. 9. 5. 오후 9:11 From Lithium to Potassium - EPRI Journal | EPRI Journal

Solution Shows Promise to Avoid Unexpected Shutdowns Due to a Vulnerable Supply of a Key Chemical

By Mary Beckman

EPRI Gears Up to Demonstrate a New Chemical for pH Control

A chemical used in Western nuclear plants for pH control is vulnerable to shortages, and EPRI is investigating its replacement with a more abundant chemical. Results to date are promising. "Good pH control is a key part of how we operate our plant," said Jim Connolly, chief nuclear officer at South Texas Project. "EPRI is the perfect organization to help industry through this issue."

One critical task for nuclear plant operators is to make sure that the water used to cool the reactor core doesn't become acidic to the point of damaging plant materials and fuel. Early in the development of pressurized water reactors, engineers selected chemicals that could be added to the water to maintain the proper pH. For the Russian-made *WWER* type pressurized water reactors, they chose potassium hydroxide. For Western pressurized water reactors, they opted for lithium hydroxide *enriched* with the lithium-7 isotope.

Fast forward many decades, and China and Russia are the only producers of enriched lithium-7. A 2013 U.S. General Accountability Office report flagged concerns about reliance on just two suppliers. In 2014, a mechanical malfunction at a Chinese production plant resulted in a global shortage of lithium-7 hydroxide.

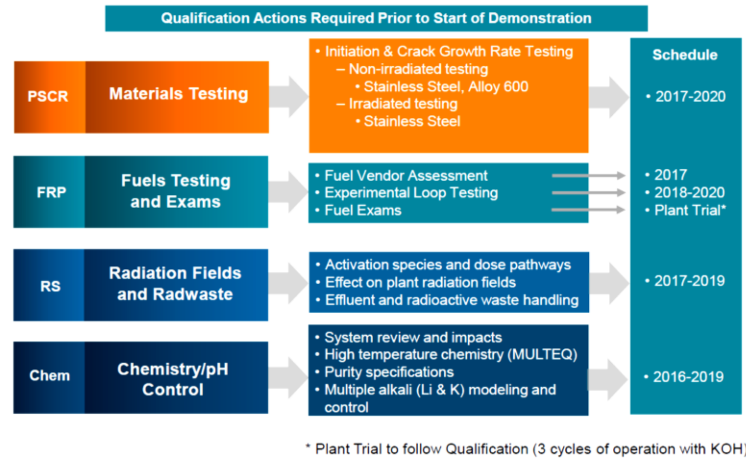
https://eprijournal.com/from-lithium-to-potassium/ 1/5

- Major supplier of ^7LiOH in past 40 years → Chinese & Russia
- Global supply shortage concern of ^7LiOH due to a mechanical malfunction of Chinese production plant at 2013.

- Increase of Li demand and price in various applications

- Explosive extension of electronic vehicle industry
- Li consumption has abruptly increased and its price increase

- KOH qualification program by EPRI consortium



- **STS and Nickel Alloy Performance:** SCC (Stress Corrosion Cracking) tests in crack initiation and growth to evaluate material integrity under specific conditions in KOH.
- **Fuel Cladding Performance:** Zirconium alloy integrity (corrosion) and CRUD deposition results showed positive evaluations in KOH studies.
- **pH control**: Multiple alkali (Li, K) modeling and control research focused on optimizing pH control in nuclear reactors using MULTEQ upgrade

Research Objectives

Objectives : Comparison of main system materials in simulated primary coolant of Li-B and K-B environments

- **Target materials :** Alloy 690TT (steam generator), Stainless steel 304 (internal, piping),
- **Experimental evaluation**:

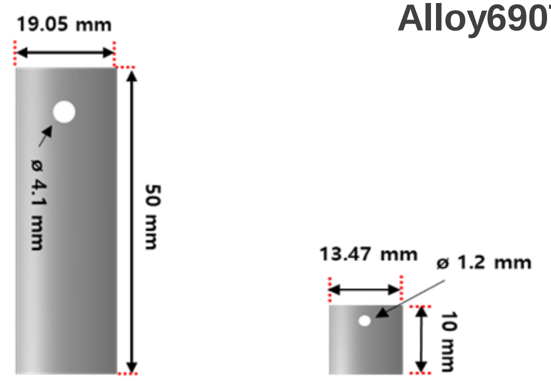
- Dissolved oxygen & dissolved hydrogen concentration : equivalent to primary coolant conditions of PWR
- Temperature and pressure : average temp. of primary coolant and 130 bar
- Chemistry and pH : B 1,000 ppm, Li 2.9 ppm and K 16.4 ppm for pH_{320^oC} 7.4
- Analysis of corroded specimens : Corrosion and release rate, Oxide morphology and chemical composition, etc.

Experimental methods (1 / 3)

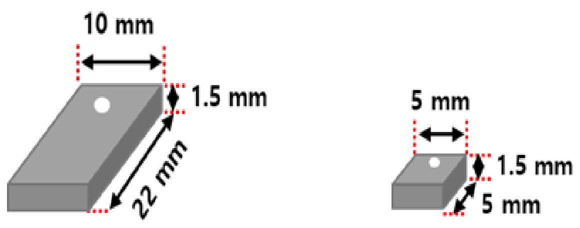
➢ Preparation of specimens

Unit :mm

Alloy690TT



STS304



- Surface finish

• Alloy690TT and STS304 were polished with up to 2000-grit SiC paper.

➢ Chemical compositions of specimens

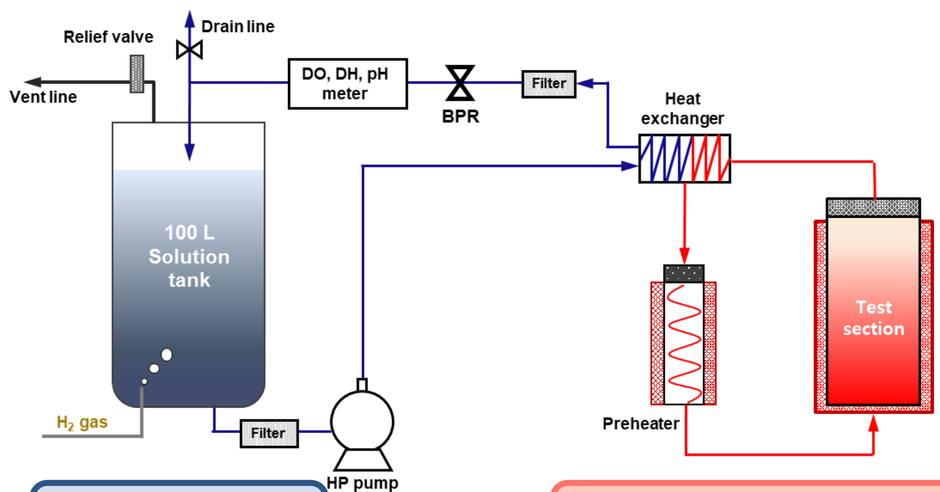
	Material	Ni	Fe	Cr	Mn
SG tube	**Alloy690TT**	**Bal.**	10.4	29.3	-
Internal, piping	**STS304**	8.0	**Bal.**	18.3	1.0

Experimental methods (2 / 3)

➢ Experimental conditions for simulation of primary water chemistry

	Li (ppm)	K (ppm)	B (ppm)	$pH_{320℃}$	Flow (cc/min)	DO (ppb)	DH (cc/kg)	Temp. (℃)	P (bar)	Time break (h)
Test 1 (Li Loop)	2.9	-	1000	7.4	60	< 5	35	320	130	300, 1000, 1500, 2000
Test 2 (K Loop)	-	16.4								

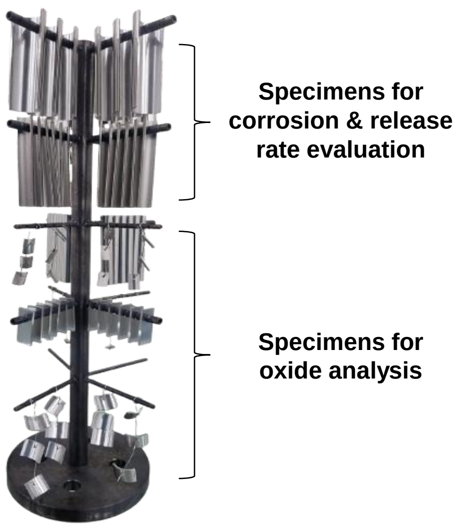
Schematics of test equipment



Primary water
Li-B or K-B

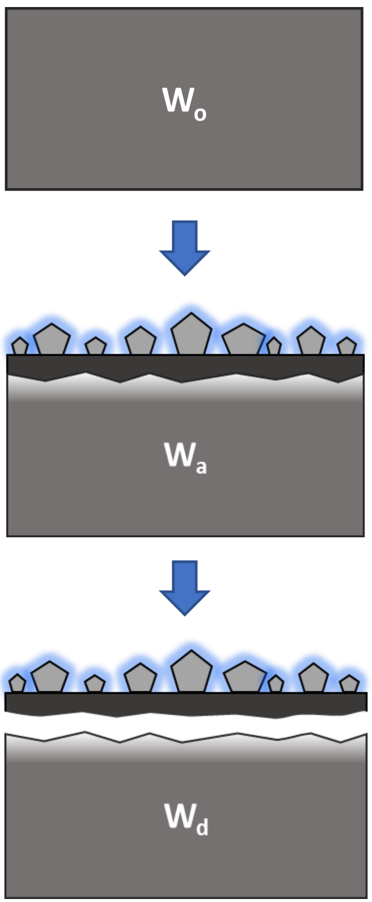
Test material
Alloy690TT, STS304

Specimen holder



Experimental methods (3 / 3)

Evaluation methods of corrosion & release rate



- **Oxide film weight (** W_{ox}) = $W_a - W_d$
- **Metal release (** W_r) = ($W_o - W_d$) – $R_m W_{ox}$
- **Corrosion rate =** $W_o - W_d$ / (A x T)
- **Release rate =** W_r / (A x T)

D = density

A = surface area

T = exposure time in primary coolant

- **Total metal corroded weight =** $W_o - W_d$

W_o = original metal weight
W_a = weight of corroded specimen
W_d = weight of metal after descaling
W_{ox} = weight of corroded oxide
R_m = metal fraction in corroded oxide
R_o = oxygen fraction in corroded oxide

Analysis of corroded specimens

➢ **Analysis methods**

- **Surface analysis**

  : Evaluation of the formation and thickness of the oxide film using SEM.

- **Compositional analysis**

  : EDS is used to determine the elemental composition and distribution of the oxide film.

- **Crystal structure analysis**

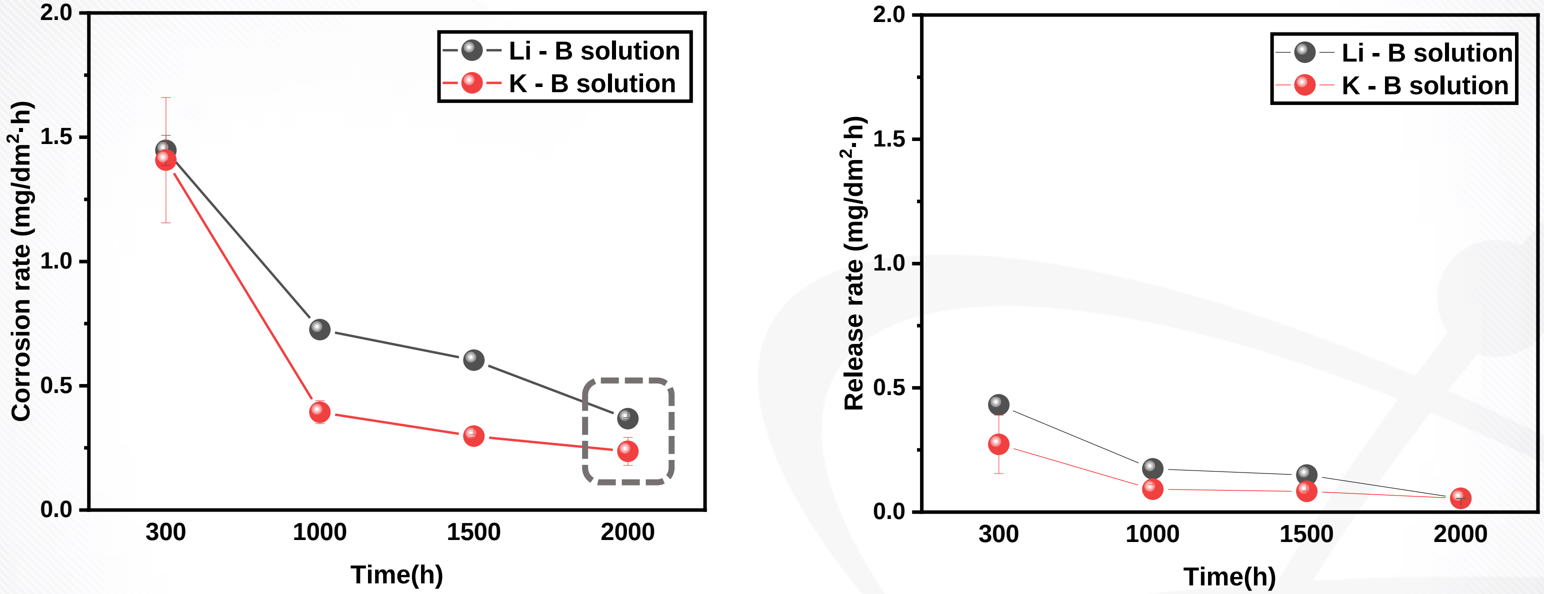
  : XRD is used to analyze the crystal structure of the oxide film.

- **XPS depth profiles**

  : analyzing the chemical state of elements in an oxide film

Results & Discussion (1 / 9)

➢ **Corrosion rate & Release rate of Alloy690TT in Li-B and K-B solution**



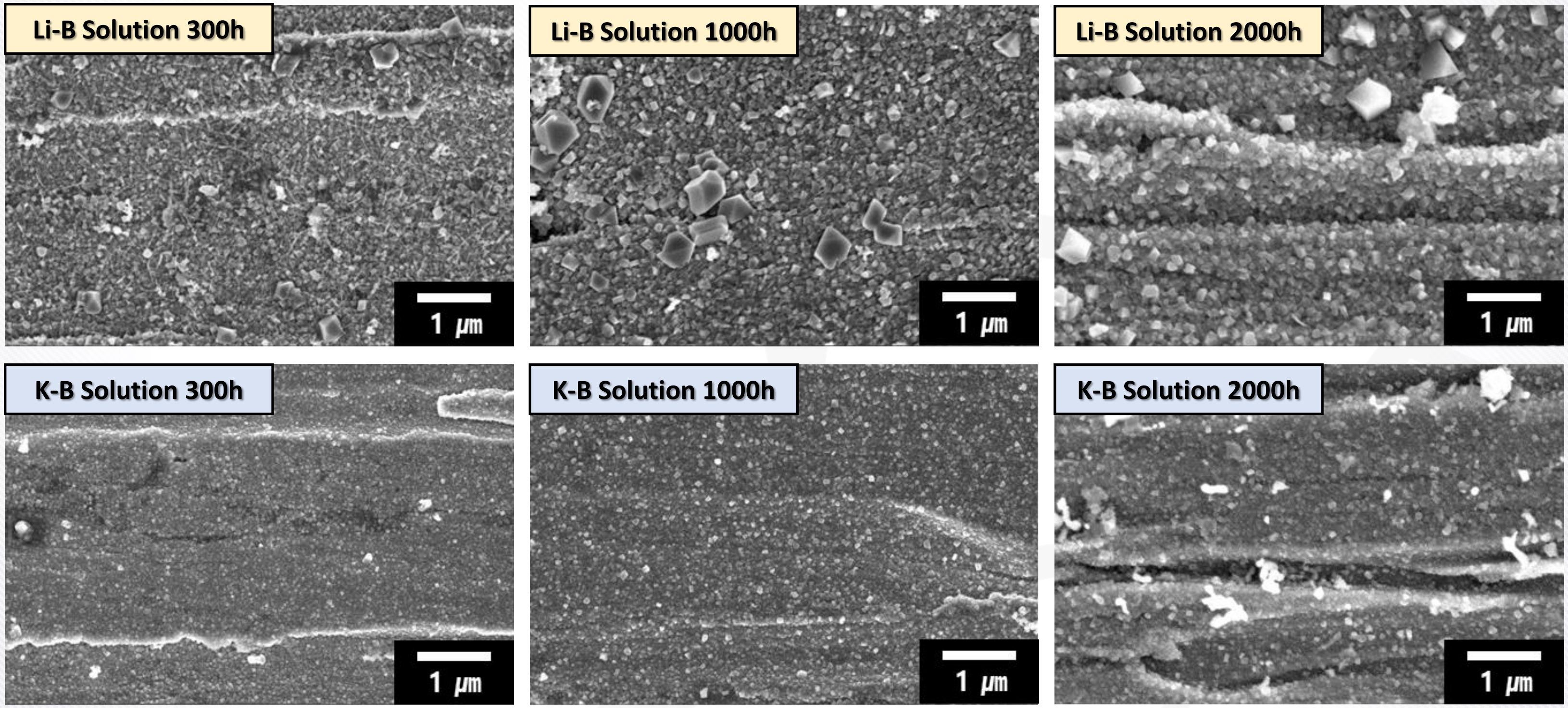
mg/dm^2h	Corrosion rate			
	300	1000	1500	2000
Li	1.44	0.72	0.60	0.36
K	1.40	0.39	0.29	0.23

mg/dm^2h	Release rate			
	300	1000	1500	2000
Li	0.43	0.17	0.14	0.05
K	0.27	0.09	0.08	0.05

- Corrosion rate exhibited exponential decline with increasing time
- Corrosion & Release rate were slightly higher in the Li-B specimen than in the K-B specimen
- The corrosion rate of Li-B specimen was found to be 36% greater than in the K-B specimen after 2000h of testing

Results & Discussion (2 / 9)

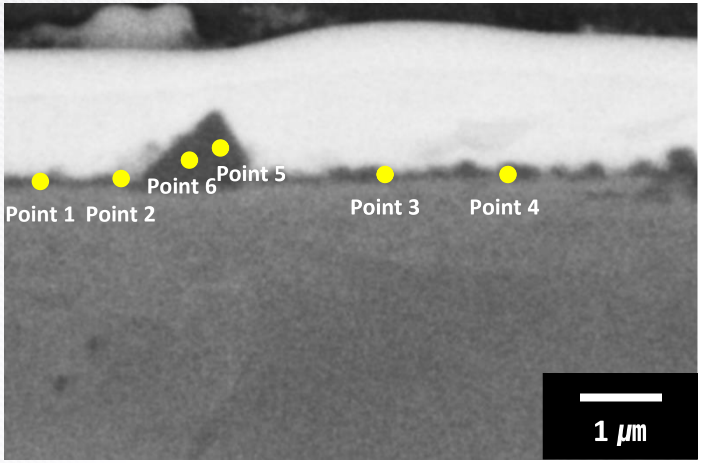
➢ **Oxide morphology of Alloy690TT after general corrosion experiment**

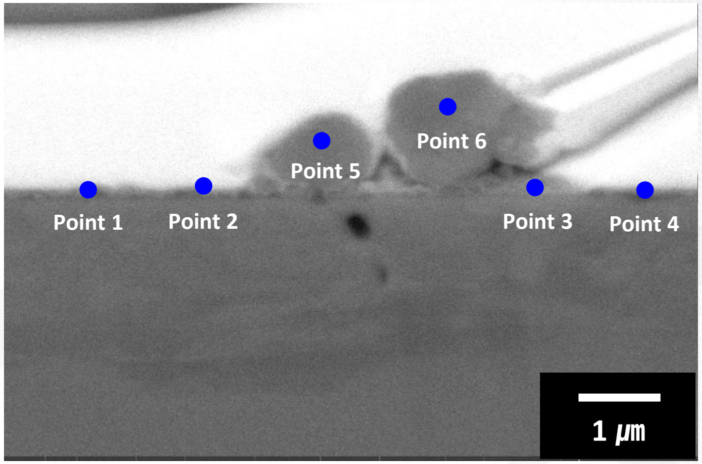


- Size of the outer oxide gradually increased with increasing time (300, 1000, 2000 h).
- Outer oxides with a polyhedral shape were formed both Li-B and K-B specimen
- In addition, needle-like oxide was formed on the surface of Alloy690TT in the Li-B after 300h of testing

Results & Discussion (3 / 9)

➢ **Cross-sectional microstructure of oxide layer formed on the Alloy690TT surface**





Point EDS

Point EDS	Chemical composition (At%)				
	O	Cr	Fe	Ni	Total
1	21.22	19.66	11.62	47.5	100
2	8.92	20.13	10.97	59.99	100
3	6.2	22.07	12.27	59.46	100
4	5.86	21.85	11.69	60.6	100
5	15.51	20.07	12.33	52.09	100
6	10.18	18.47	12.58	58.76	100
avg.	11.315	20.375	11.91	56.4	100

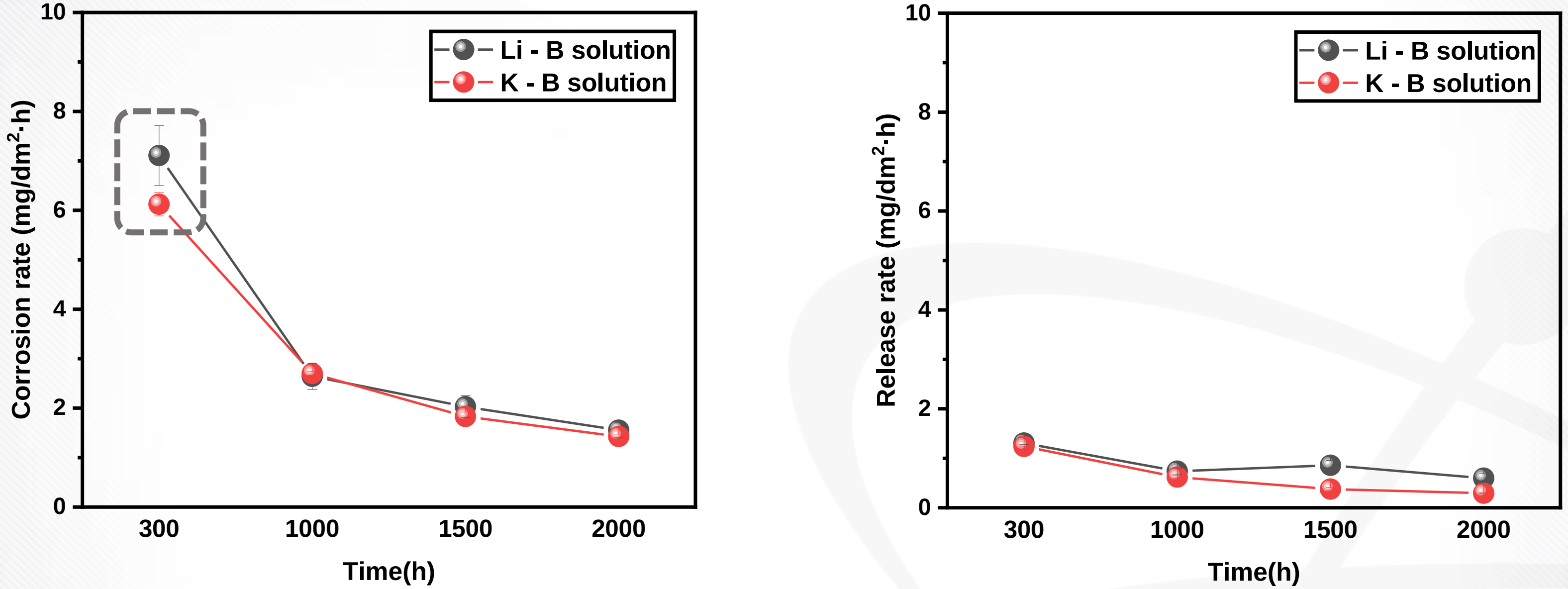
Point EDS

Point EDS	Chemical composition (At%)				
	O	Cr	Fe	Ni	Total
1	16.04	18.7	15.34	49.92	100
2	12.1	20.31	13.13	54.46	100
3	15.47	23.63	11.16	49.74	100
4	10.3	20.7	12.28	56.72	100
5	3.9	5.87	2.95	87.28	100
6	2.84	4.85	3.23	89.08	100
avg.	10.10	15.67	9.681	64.53	100

- In Li-B and K-B specimens, inner oxide layer higher atomic percentage of Cr than outer oxide layer
- Li-B and K-B specimens formed Cr-rich oxide layer of less than 200nm

Results & Discussion (4 / 9)

- **Corrosion rate & Release rate of STS304 in Li-B and K-B solution**



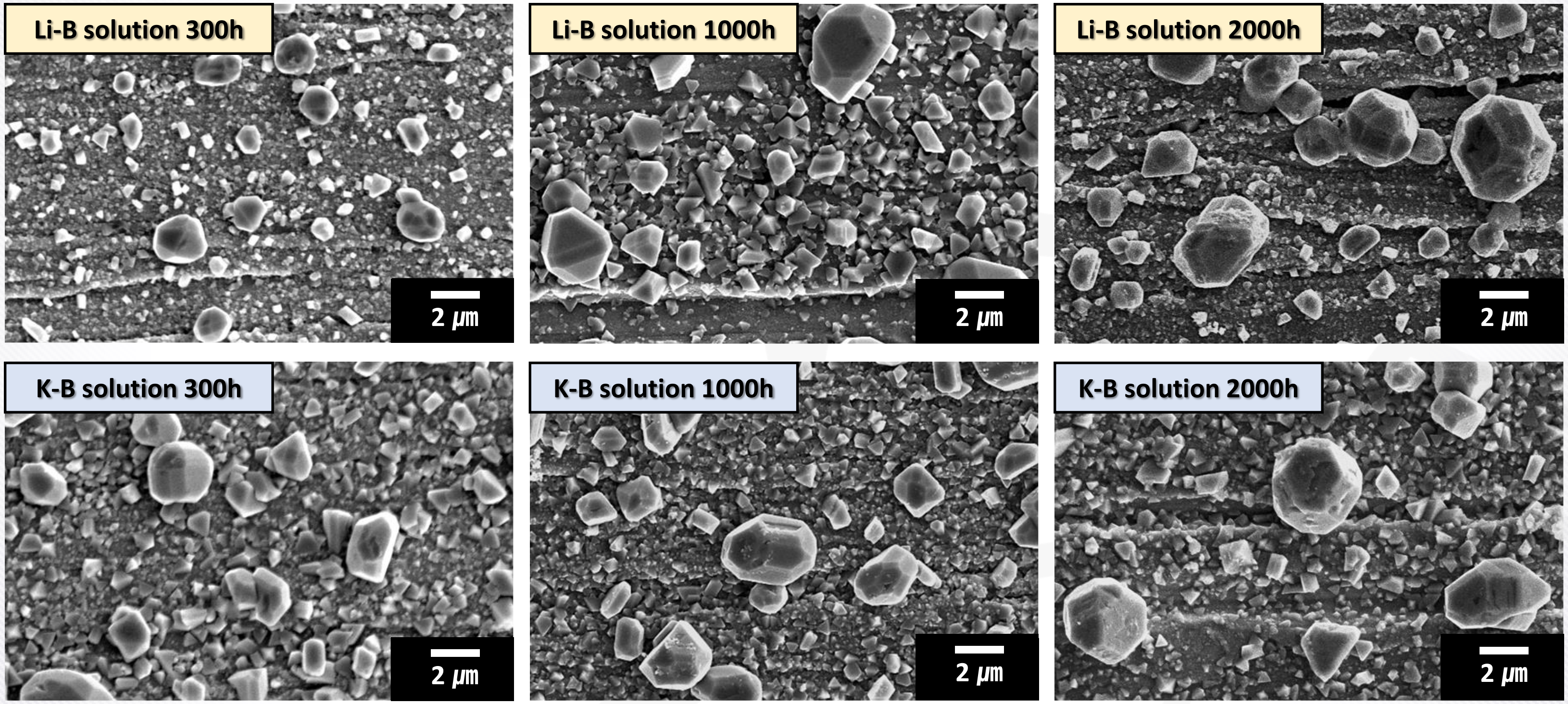
mg/dm^{2}h	Corrosion rate			
	300	1000	1500	2000
Li	7.10	2.64	2.02	1.55
K	6.12	2.70	1.83	1.42

mg/dm^{2}h	Release rate			
	300	1000	1500	2000
Li	1.30	0.73	0.85	0.59
K	1.23	0.61	0.37	0.29

- Corrosion rate exhibited exponential decline with increasing time
- Corrosion & Release rate were slightly higher in the Li-B specimen than in the K-B specimen
- The difference in corrosion rate between Li-B and K-B specimen was approximately 14% after 300h of testing

Results & Discussion (5 / 9)

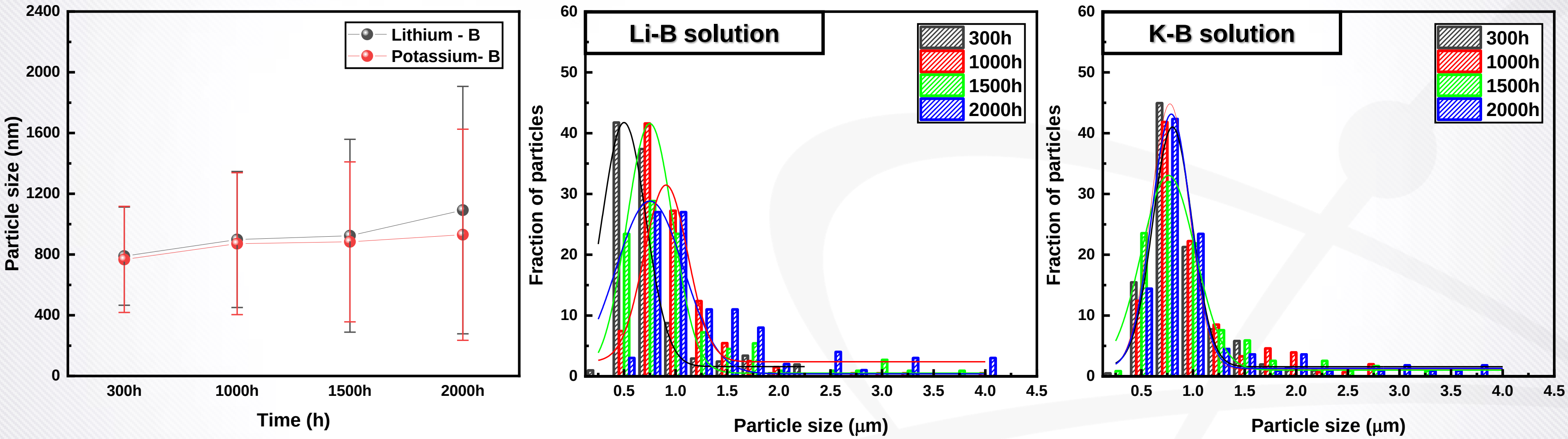
➤ **Oxide morphology of STS304 after general corrosion experiment**



- Particle oxide size gradually increased with increasing time (300, 1000, 2000 h)
- Outer oxides with a polyhedral shape were formed both Li-B and K-B Specimen

Results & Discussion (6 / 9)

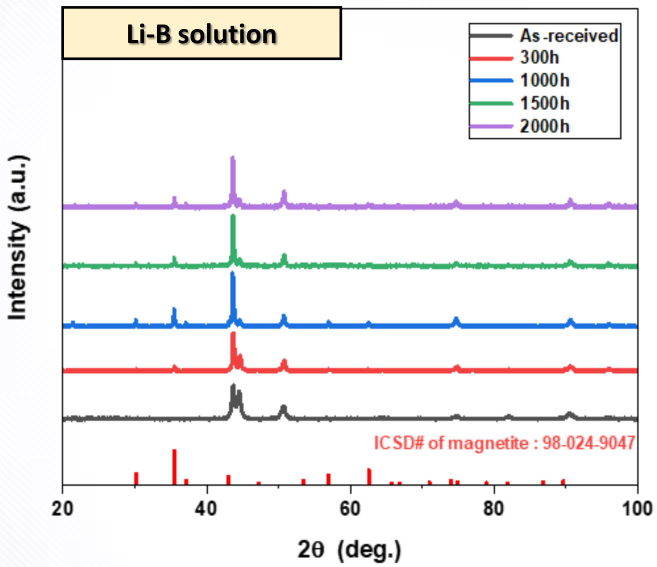
➢ **STS304 outer oxide particle size distribution in Li-B and K-B specimen**

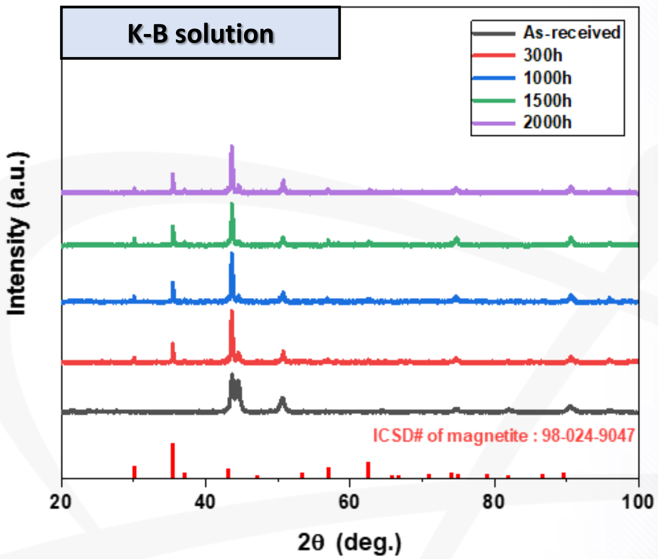


- Outer oxide particle size was measured to exhibit the distribution with Gaussian function
- Li-B and K-B specimens exhibit a gradual increase in particle size over time
- Outer oxide particle size measured in the Li-B specimen was generally larger than in K-B specimen
- Considering the corrosion rate and the size of the outer oxide film, Li-B can be more corroded than K-B.

Results & Discussion (7 / 9)

➤ **XRD and SEM-EDS Results of STS304 after general corrosion experiment**

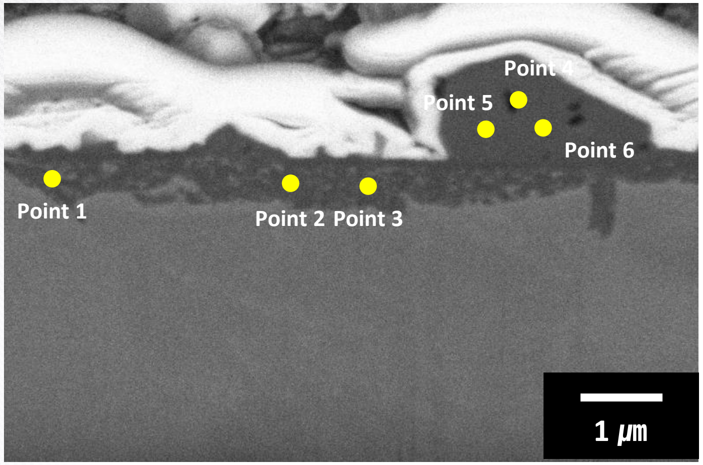


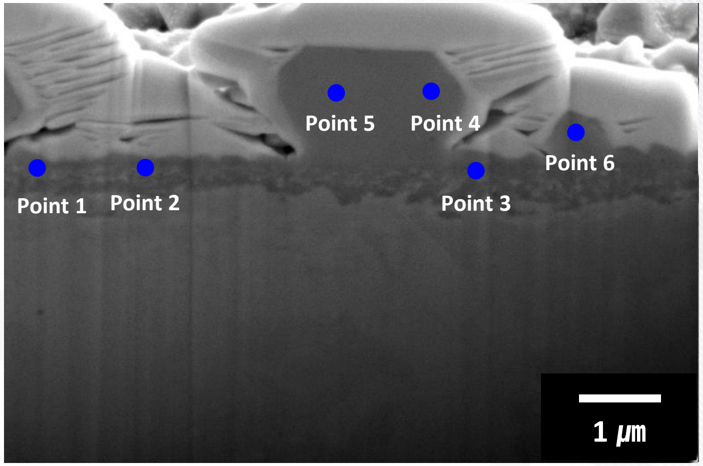


- Characteristic magnetite peak ICSD#: 98-024-9047 is observed in both Li-B and K-B specimens and the metal peak around 45 degrees tends to decrease with increasing corrosion time.
- Li-B and K-B specimens, characteristic peaks of the oxide film were observed around 30 and 35 degrees.

Results & Discussion (8 / 9)

➢ **Cross-sectional microstructure of oxide layer formed on the STS304 surface**





Point EDS

Point EDS	Chemical composition (At%)				
	O	Cr	Fe	Ni	Total
1	36.81	20.83	36.41	5.94	100
2	34.99	20.71	38.51	5.79	100
3	34.63	19.65	38.48	7.24	100
4	31.39	15.1	45.59	7.92	100
5	49.16	4.53	37.48	8.83	100
6	46.51	3.51	40.53	9.45	100
avg.	38.91	14.05	39.50	7.52	100

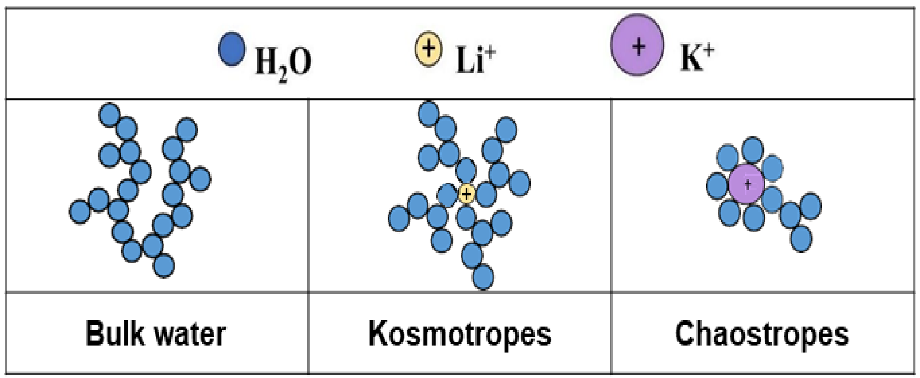
Point EDS

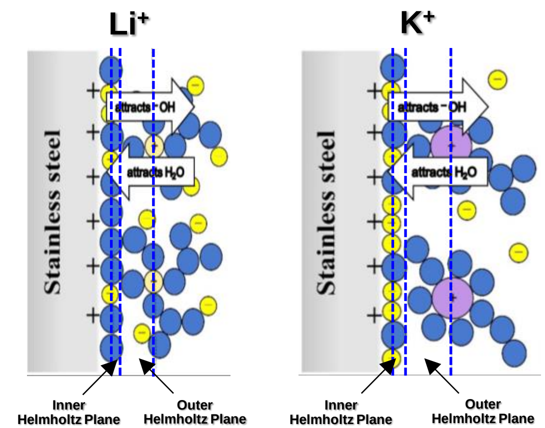
Point EDS	Chemical composition (At%)				
	O	Cr	Fe	Ni	Total
1	44.19	18.73	28.89	8.19	100
2	41.94	18.81	30.49	8.75	100
3	23.88	17.78	45.91	12.43	100
4	57.49	3.35	37.54	1.62	100
5	59.81	1.95	37	1.24	100
6	60.37	1.86	36.67	1.1	100
avg.	47.94	10.41	36.08	5.55	100

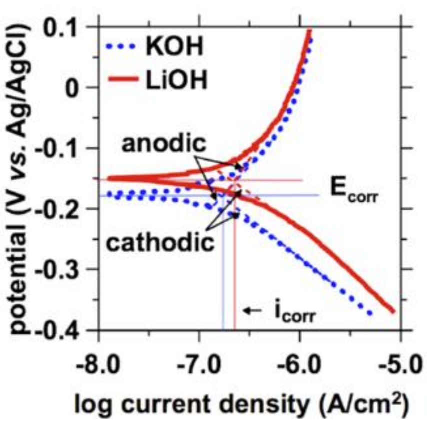
- Inner oxide layer of Li-B specimen is 20 percent thinker than K-B specimen
- Inner and outer oxide layer have high atomic percentage of oxygen in Li-B and K-B specimen

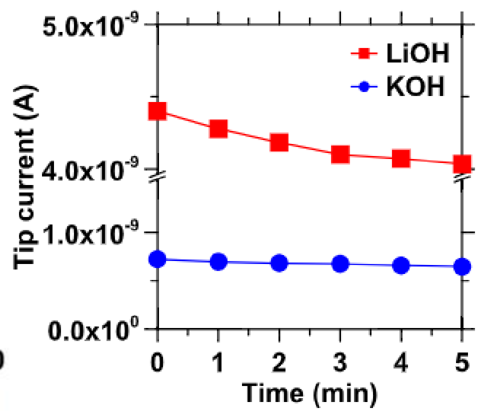
Results & Discussion (9 / 9)

➢ **Effect of Li⁺ and K⁺ Ion Radii on Corrosion Characteristics**









- corrosion current density (icorr) under immersion in 10 mM LiOH is 2.03 × 10^{-7} A/cm^2 ,which is slightly higher than that in 10 mM KOH (icorr = 1.55× 10^{-7} A/cm^2).
- differences in the initial currents observed in solutions of LiOH (4.5 × 10^{-9} A) and KOH (0.7× 10^{-9} A),

Conclusions

- Oxide layer of STS304 and Alloy690TT consists of polyhedral shaped external oxides and dense internal oxide layer.

- The external oxide is a $Ni_xFe_{3-x}O_4$ (nickel ferrite) for Alloy 690TT and $(Ni,Cr)_xFe_{3-x}O_4$ (almost magnetite) for STS304. In addition, the internal oxide is a (Ni, Fe)Cr_2O_3 (Cr-rich oxide) due to slow diffusion rate of Cr through preformed oxide layer.

- Corrosion and release rates of STS304 and Alloy 690TT are larger in Li-B condition than in K-B condition due to its diffusion and solubility in different ionization environment.

- KOH is acceptable to replace LiOH in PWR primary coolant with considering corrosion and release properties of STS304 and Alloy690TT.

Thank you

E-mail : hwkim95@kaeri.re.kr

KAERI Korea Atomic Energy Research Institute