Corrosion Behavior of $(Fe,Cr)_2B$ Metallic Boride of Borated Stainless Steel in Borated Water Environment

Daehyeon Park[a], Yunju Lee[a], Junhyuk Ham[a], Seung Chang Yoo[a], Yongdeog Kim[b], Kiyoung Kim[b], Donghee Lee[b], and Ji Hyun Kim[a]*

[a] *Department of Nuclear Engineering, Ulsan National Institute of Science and Technology*

[b] *Korea Hydro & Nuclear Power Corporation*

* *kimjh@unist.ac.kr*

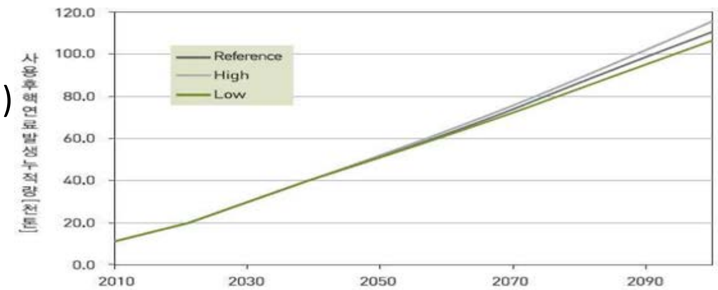
KNS, 2021 Fall

2021. 10. 22

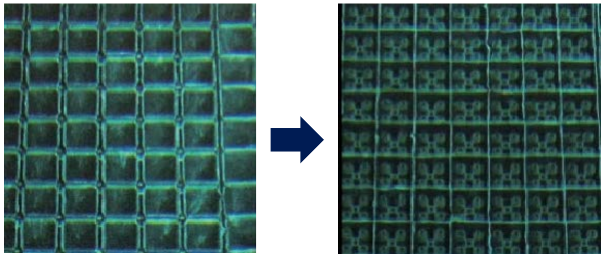
Contents

Neutron absorber in spent fuel pool

- **Neutron absorber in high-density storage rack**
  - Some spent nuclear fuel pools (SFPs) contains spent nuclear fuel (SNF) in high density, due to **limited space of SNF storage**.
  - **To maintain sub-criticality and remove the decay heat** of SNFs, neutron absorbers have been used in the form of **structure material itself (storage rack) or structural attachment**.
  - In Korea, **Borated Stainless Steel (BSS)** is often used structure material for high-density storage rack. Aluminum-based neutron absorbers such as BORAL, METAMIC, MAXUS are used for structural attachment.
  - Once the storage rack installed, it is hard to change structural material of it due to high cost and radiation problems.



Estimated amount of spent nuclear fuel in Korea



Capacity of rack increases approximately 2 times

→ **Thus, integrity and functionality of BSS should be evaluated for long term operation.**

Type of neutron absorbers

	BSS	BORAL	METAMIC	MAXUS
Type	structural	attachment	attachment	attachment
Installation sites	Kori 3, Hanbit 3, 4,	Kori, Hanul, Hanbit, Shin-Wolsung, Shin-Kori, etc.	Hanul 3, 4, Hanbit 2	Shin-Kori 1, 2
Base material	SS304	Al 1100 (Al-0.12Cu), Al 1100, B_4C	Al 6061 (Al-0.6Si-0.28Cu-1.0Mg-0.2Cr), B_4C	Al 5052 (Al-2.5Mg-0.25Cr), Al 1070 (Al>99.7), B_4C
Possible problems	Decrease of ductility due to intergranular attack	Swelling (NRC IN 2009-26)	B_4C leaking due to corrosion of aluminum near B_4C on surface	Pitting corrosion for dry storage application

Borated stainless steel in spent nuclear fuel pool

- **Environment of spent nuclear fuel pool**
  - Maintaining the spent fuel pool boric acid water temperature < 60°C by removing the decay heat input from the fuel assemblies.
  - In Korea, the water environment of spent fuel pool which using structural material BSS maintain boron concentration according to operating standard.
- **Microstructure of BSS**
  - Since solubility of boron in austenite structure is quite low, boron are added in the form of metallic boride ($(Fe,Cr)_2B$). During formation of it, Cr contents in substrate are decreased[2].

BSS, SS 304 composition[1]

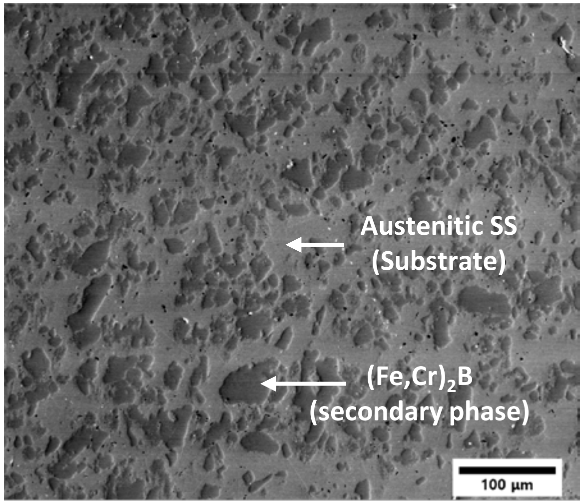
Type	Fe	Cr	Ni	C	Mn	P	S	Si	N	B
304B7	Bal	18.0~20.0	12.0~15.0	0.08	2.00	0.045	0.03	0.75	0.1	1.75

Type	Fe	Cr	Ni	C	Mn	P	S	Si	N
SS 304	Bal	18.0~20.0	8.0~11.0	0.08	2.00	0.045	0.03	0.75	0.1

Boron Content(%) : 0.20, 0.30, 0.50, 0.75, 1.00, 1.25, 1.50, 1.75

Hardness, tensile strength, yield strength →

← Ductility, toughness, corrosion resistance

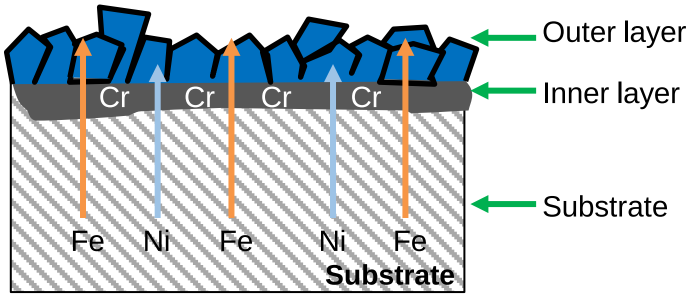


SEM image surface of BSS

[1] ASTM International. "ASTM A887-89 (2004): Standard Specification for Borated Stainless Steel Plate, Sheet, and Strip for Nuclear Application." Published on CD-ROM. West Conshohocken, Pennsylvania: ASTM International. 2008.
[2] D.A.Moreno et al., corrosion vol.60, No.6,(2004)

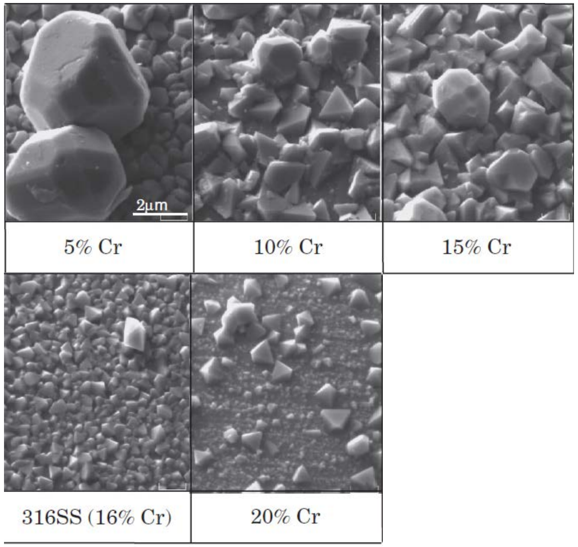
Major corrosion type of BSS

- **Corrosion Behavior of BSS [1,2]**
  - BSS is known to have similar general corrosion behavior because it is based on SS304 composition.
  - One of the major corrosion characteristics of stainless steel, the Cr oxide layer, forms a passivation oxide film have high corrosion resistance of stainless steel.
  - However, **Cr oxide formation in substrate of BSS could be delayed or unstable** due to **low Cr contents** in it.
  - Cr contents are 12 w.t. % in substrate and 45 w.t. % in secondary phase.
  - The corrosion rate decreased with increasing chromium content in the alloys due to the chromium-enriched inner layer acting as a diffusion barrier.

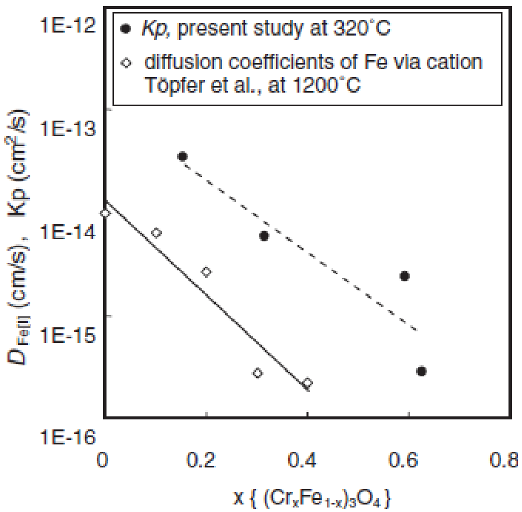


- Cr : high oxidation power
- Fe > Ni : diffusion outside

Corrosion behavior of stainless steel



SEM images of the oxide film after immersion in simulated PWR primary water at 320C for 380 h



Relationship between the diffusion rate of iron via cation interstitials and chromium fraction in spinel oxide,

[2] D.A.Moreno et al., corrosion vol.60, No.6,(2004)
[3] Kuang, W., Han, E. H., Wu, X., & Rao, J. (2010).
[4] Duan, Z., Arjmand, F., Zhang, L., & Abe, H. (2016).
[5] T. TERACHI et al., Journal of Nuclear science and technology, Vol.45, No 10, p. 975-984(2008)

Experimental

Long-term accelerated corrosion of BSS → Analysis of microstructure and major corrosion of BSS → Corrosion behavior of BSS in SFP environment

- **Experimental condition**
  - **Acceleration coefficient is determined to 30** with 25 ℃ of aging temperature and 250 ℃ of service temperature.
  - Using circulation loop system, accelerated corrosion experiment was conducted in simulated SFP condition.

SFP environment at Kori unit 3, Hanbit unit 3 and 4

Boron	DO	Temperature in SFP	Operating time
4200 ppm	~ 8000 ppb (Open pool)	25 ℃	60 years

Accelerated corrosion test condition[7]

Boron	DO	Temperature in test section	Accelerated coefficient
4200 ppm	2000 ppb	250 ℃	X 30

Fig. Accelerated corrosion loop system

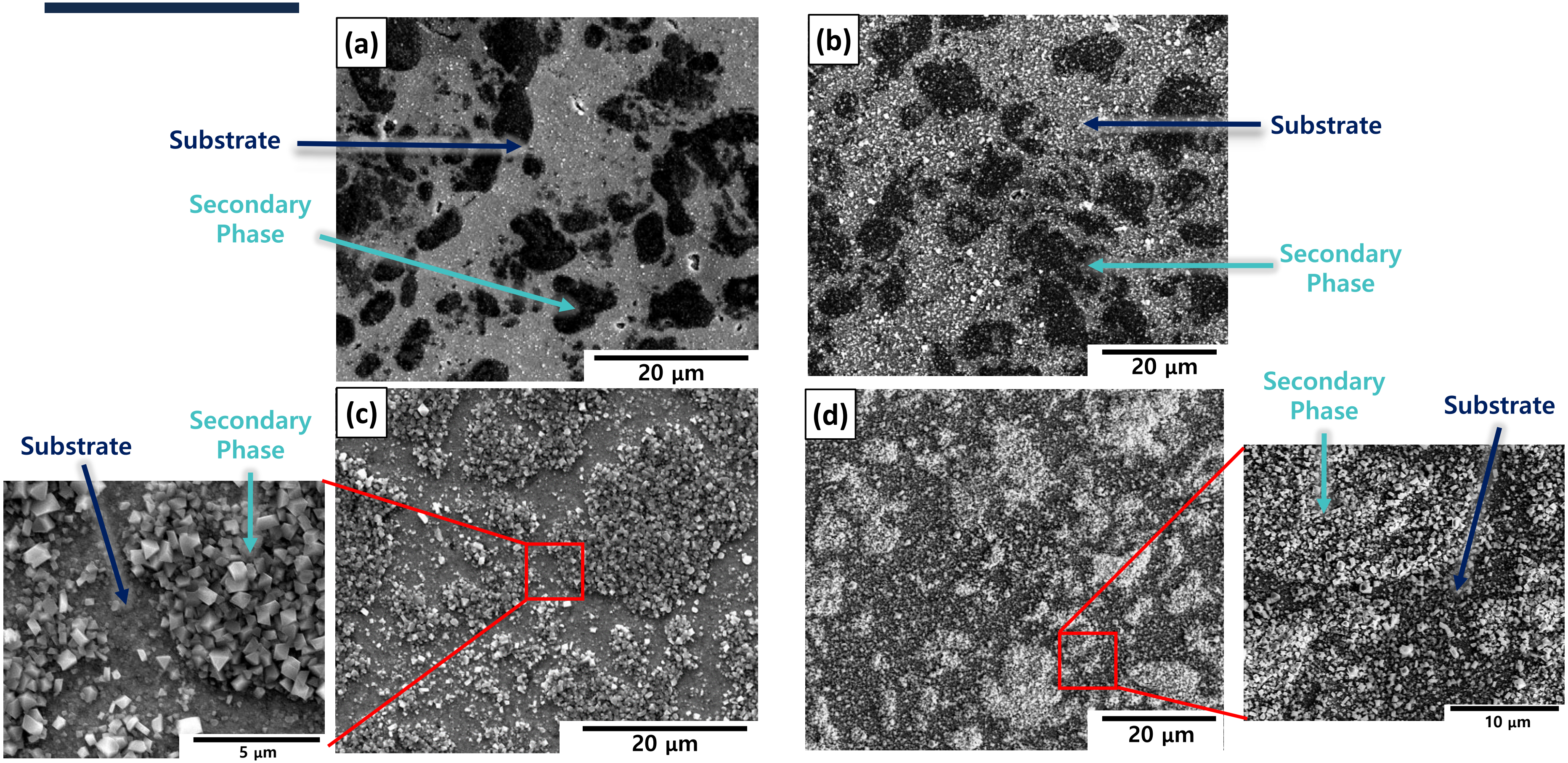
- **Specimen and exposure time**
  - 20 mm X 20 mm X 3 mm BSS coupon exposed for **0.2, 2, 4, 6, 8, 12**, 18, 24 **months**, respectively.

BSS Chemical composition [w.t.%]

Type	Fe	Cr	Ni	C	Mn	P	S	Si	N	B
304B7	Bal	20.28	13.32	0.011	1.3	0.01	<0.0003	0.29	0.029	2.07

[6] Daehyeon Park et al., Corrosion Behavior of Borated Stainless Steel in High DO-Borated Water Environment, KNS spring (2021)

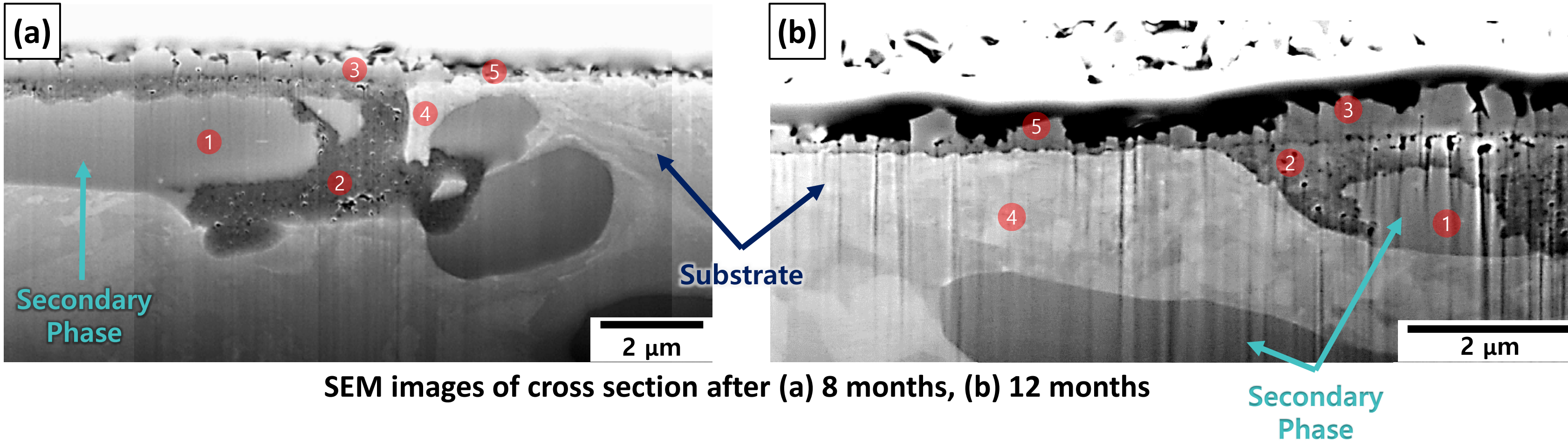
Morphology of surface



SEM images of surface after (a) 0.2 months, (b) 4 months, (c) 8 months and (d) 12 months

- The oxide film grown into a polyhedral structure after 6 months grew in a secondary phase larger than the substrate.

Cross section of BSS



SEM images of cross section after (a) 8 months, (b) 12 months

EDS result of upper images after (a) 8 months, (b) 12 months

(a)

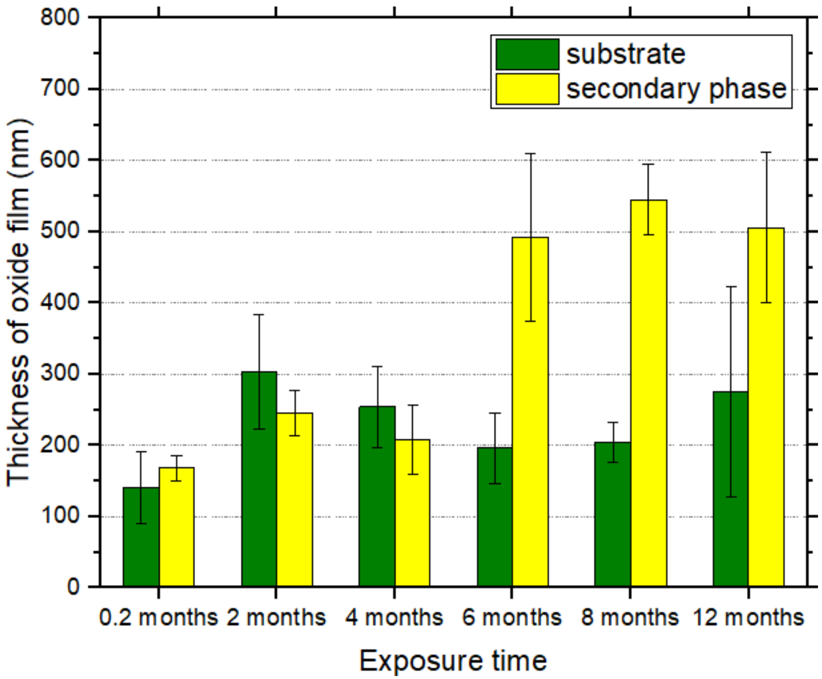
Element(a.t.%)		*O*	*Cr*	*Fe*	*Ni*
Secondary phase	1	7.64	54.8	36.03	1.53
Oxidized secondary phase	2	26.18	14.1	56.28	3.44
Secondary phase oxide film	3	27.91	17.85	36.55	17.68
Substrate	4	5.86	22.84	60.05	11.25
Substrate oxide film	5	7.24	18.86	55.45	18.46

(b)

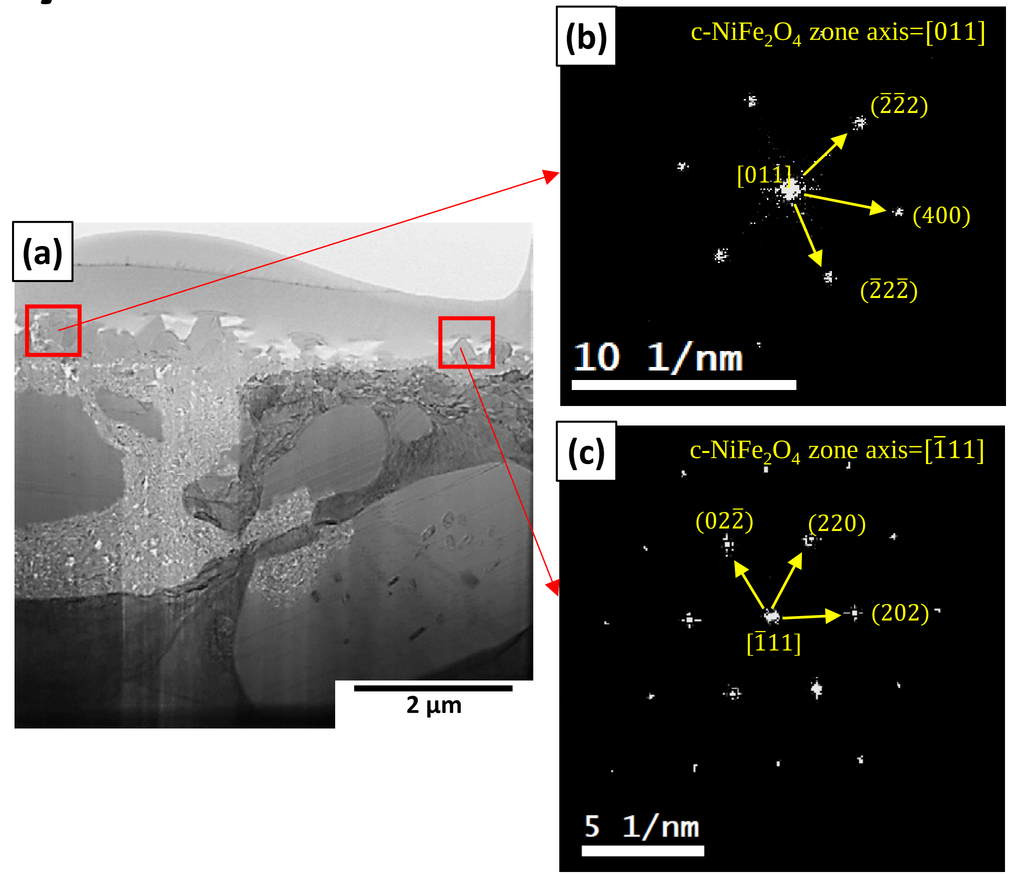
Element(a.t.%)		*O*	*Cr*	*Fe*	*Ni*
Secondary phase	1	10.29	61.56	24.91	3.25
Oxidized secondary phase	2	43.24	18.68	28.48	9.61
Secondary phase oxide film	3	34.41	14.59	23.91	27.1
Substrate	4	8.11	25.69	53.52	12.68
Substrate oxide film	5	30.47	10.82	29.13	29.58

- Secondary phase oxidized more than substrate and **formed porous structure**.
- **Oxide film thickness of the secondary phase grew thicker** than the substrate.
- And oxidized secondary phase contains **higher Fe and lower Cr** contents than secondary phase.
- Further analysis on **structure of oxide film** and **chemical composition of oxidized secondary phase** was conducted.

Oxide film - thickness and crystal structure



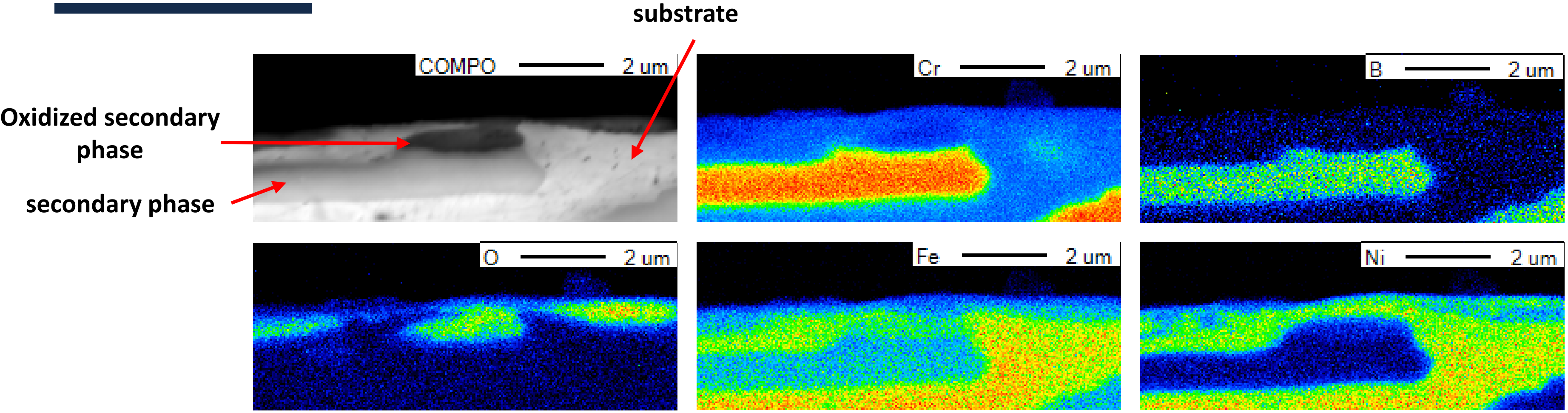
Oxide thickness formed on substrate and secondary phase over exposure time



(a) STEM images of the cross section of BSS which exposed for 8 months
Diffraction pattern image (b) secondary phase oxide film, (c) substrate oxide film

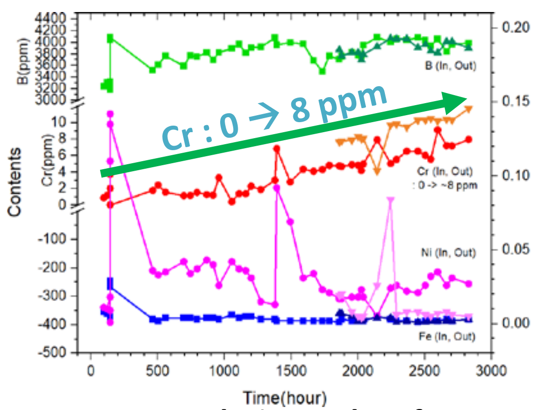
- At 6 months exposed specimen, the oxide film on the secondary phase was thicker than that on the substrate.
- Crystal structure of secondary phase and substrate oxide film is $NiFe_2O_4$.
- Porous media of oxidized secondary phase could enhance the outward diffusion of metal ions.

Oxidized secondary phase – chemical composition

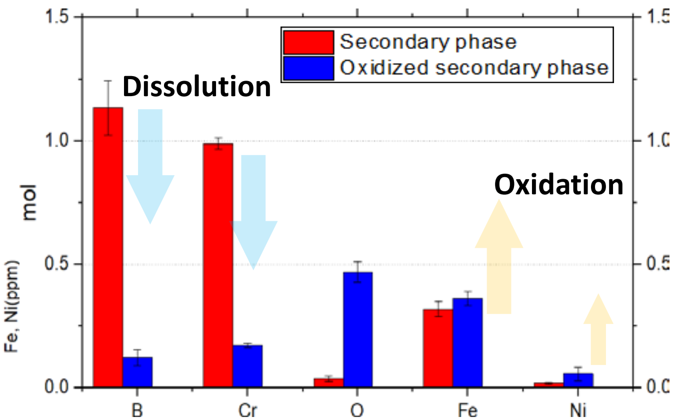


EPMA mapping analysis of BSS which exposed for 8 months

- From ICP-OES analysis results, Cr concentration in water increased to **8 ppm**.
- In oxidized secondary phase, **B and Cr are significantly decreased** while Fe and Ni slightly increased.



ICP-OES analysis results of water



Comparison of elements before and after oxidation of secondary phase

Oxidation of boron in the BSS

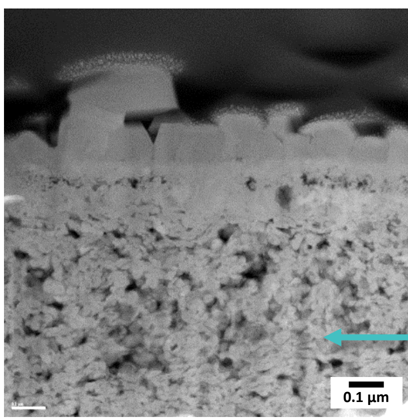
- If refer to the Ellingham diagram, boron itself has very high oxidation power in oxidizing environments.

- Oxide Priority

$$B_2O_3 \rightarrow Cr_2O_3 \rightarrow Fe_3O_4 \rightarrow Fe_2O_3$$

- Boron is oxidized and the secondary phase is corroded before the formation of Cr oxide film, which is passivation layer.
- B_2O_3 is soluble in water environment.

$$CrB_2 + 6H_2O = Cr^{2+} + 2H_3BO_3 + 6H^{+} + 8e^{-}$$



Oxidized secondary phase (porous structure)

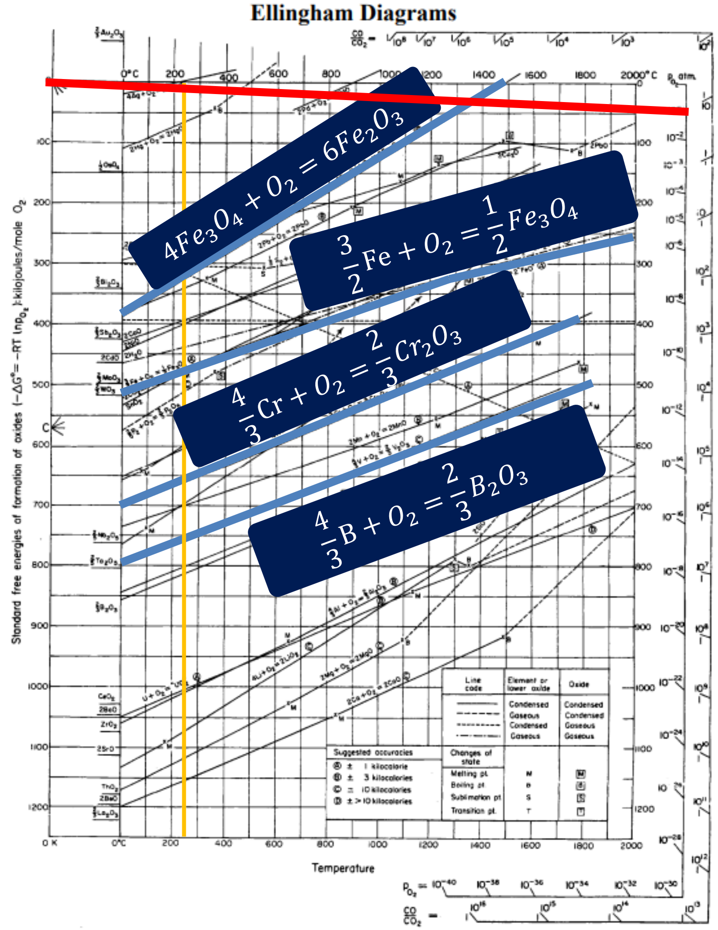


Fig. Ellingham diagram

The secondary phase is oxidized to form a porous structure. The porous structure becomes a diffusion path, and Ni and Fe in the surrounding substrate diffuse to form an oxide film.

[7] L. R. Jordan et al., Corrosion and passivation mechanism of chromium diboride coatings on stainless steel, Corrosion science 47, (2005)

Summary and future work

- **Summary**

- Borated stainless steel / accelerated corrosion test in SFP environment / 0.2, 2, 4, 6, 8, 12 months

Focus

Secondary phase, substrate oxide film / Oxidized secondary phase

- **Oxide film**
  - Oxide film thickness : Substrate < secondary phase oxide film
  - Oxide film crystal structure : $NiFe_2O_4$
- **Oxidized secondary phase**
  - Secondary phase is oxidized more than substrate.
  - As the secondary phase is oxidized, boron and chromium are dissolved and Fe and Ni slightly increased.

- **Conclusion**
  - The **secondary phase is oxidized**, and **B and Cr are dissolved** to form a **porous** form. This porous structure acts as a **diffusion path** of the surrounding substrate and, thus, **Ni and Fe become diffused** to form an oxide film.

- **Future work**

- Analysis of BSS as-received defect.
- Study the possible defects and the factors that cause them in secondary phase.

Thank you for listening

Daehyeon Park