Method of Monitoring the Corrosion Behavior on the Surface Treated FMS and CVD Coated Specimen in Liquid Sodium Environment

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Korean Nuclear Society Autumn Meeting
Pyeongchang, Korea
2014.10.31

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Outlook

Background of research

- Gr.92 and HT9 (Ferritic/martensitic steels) are considered as candidates of cladding materials of Sodium-cooled Fast Reactors (SFRs).

- Their compatibility with sodium is one of issues especially dissolution, chemical reaction, and carbon transfer with impurities, which degraded the mechanical properties in high burn-up fuel or long cycle fast reactor design.

- HT9 and Gr.92 are known as compatible in sodium environment because the usual refueling time of SFRs is designed about 54 months. In the Ultra-long Cycle Fast Reactor (UCFR) which is developed in UNIST, however, cladding is exposed long-term in high temperature liquid sodium environment

- To monitor the corrosion behavior of these candidate materials in sodium environment, Electrochemical Impedance Spectroscopy (EIS) method is first introduced and investigated in this study.

- Chemical Vapor Deposition (CVD) coating for decarburization barrier on the surface of FMS and to protect oxide formation is considered in this study.

Motivation

1. Fast reactor operation time is extended by developing Ultra-long Cycle Fast Reactor(UCFR)
2. Importance of oxide research increased in liquid sodium environment
3. Generally, research of liquid sodium oxidation is proceeding ex-situ experiment
4. The EIS method can monitor the corrosion behavior observed at the surface of the materials by in-situ

Background of research

- Reason for electrochemical impedance.

- In aqueous solution and liquid metal environment, it can be indicated that change of oxide layer thickness and corrosion resistibility by analyzing electrical signal.

- In general oxide layer research that exposure high temperature liquid sodium, it is performed ex-situ experiment. In electrical impedance research, however, it can be performed in-situ experiment.

- In this research, real-time impedance spectroscopy measurements were made continuously on one specimen during the entire sodium test to characterize the corrosion kinetics.

EIS test in LBE

- The thickness value for the oxide scale formed on the specimen surface at 1000, 2000, and 3600h immersion time in LBE are determined to be 270nm, 495nm, and 837nm. (Fig. 1)

- Figure. 2 illustrates the resulting Bode Phase plot and Nyquist plot of the specimen at three different times during the corrosion tests.

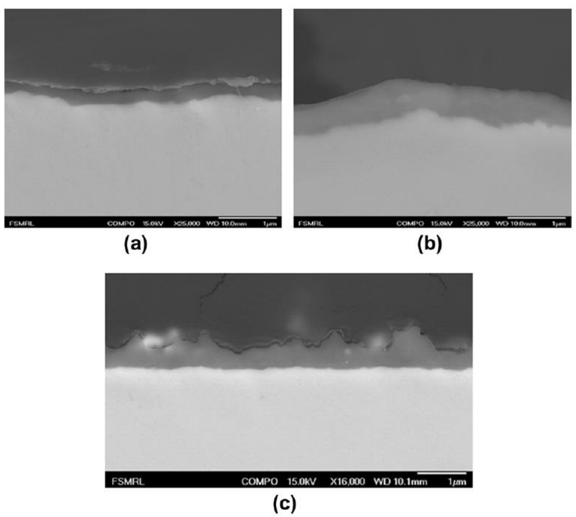


Fig. 1 SEM backscattered electron images of the oxide scale formed on FeCrAl in LBE (a) 1000h, (b) 2000h (c) 3600h immersion time.

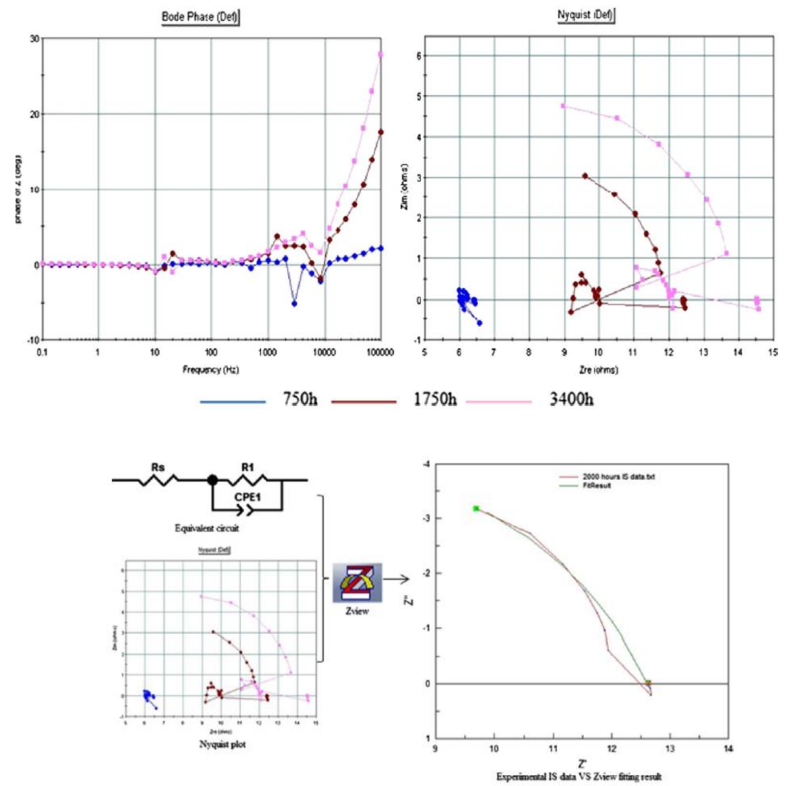


Fig. 2 Bode Phase and Nyquist plot based on the impedance data for one FeCrAl specimen at three different corrosion moments in LBE.

[1] Xiang Chen, Journal of Nuclear Materials 431 (2012) 125.

EIS test in LBE

- All the parameters can be acquired from the fitting of the Nyquist plot with Z view. Therefore the equivalent capacitance C can be calculated. The relationship between C and oxide thickness is given by

$$d = \frac{\varepsilon \varepsilon_0 S}{C}$$

- where ε is the dielectrical constant of Al_2O_3 (10.8) and ε_0 is vacuum permittivity, S is the electrode area which equals to the surface exposure area of the specimen in sodium.

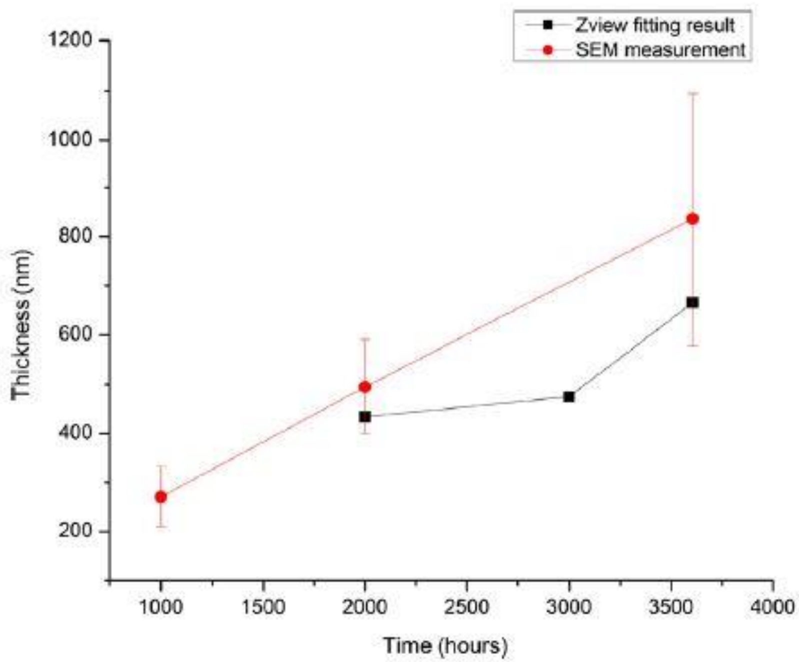


Fig. 1 Comparison of oxide thickness derived from impedance data and SEM measurement

[1] Xiang Chen, Journal of Nuclear Materials 431 (2012) 125.

Objective and Approach of research

Objective

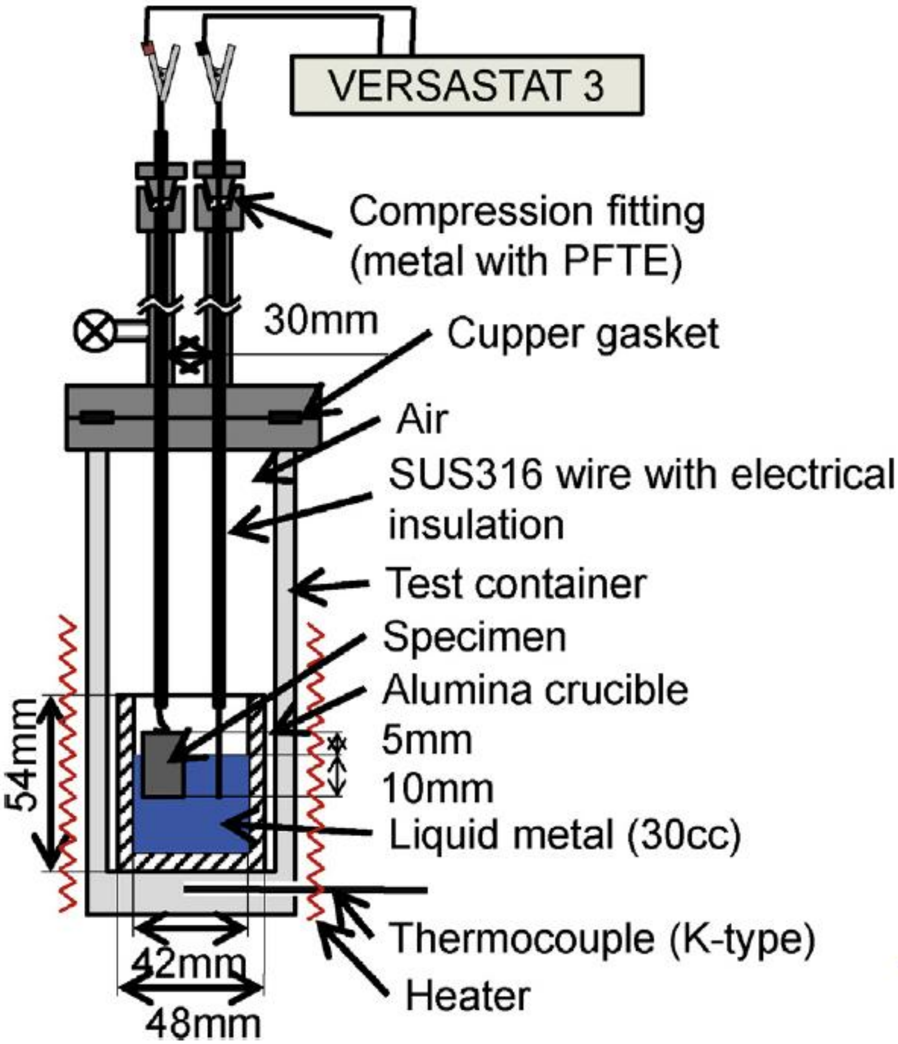
- **(Final Goal) It is to monitor the corrosion behavior of these candidate materials in sodium environment.**
- It can be contributed to corrosion modeling in liquid sodium.
- **(Final Goal) CVD coating of SiC and Si3N4 can protect the decarburization barrier on the surface of FMS.**
- It can be measured by electrochemical impedance spectroscopy.

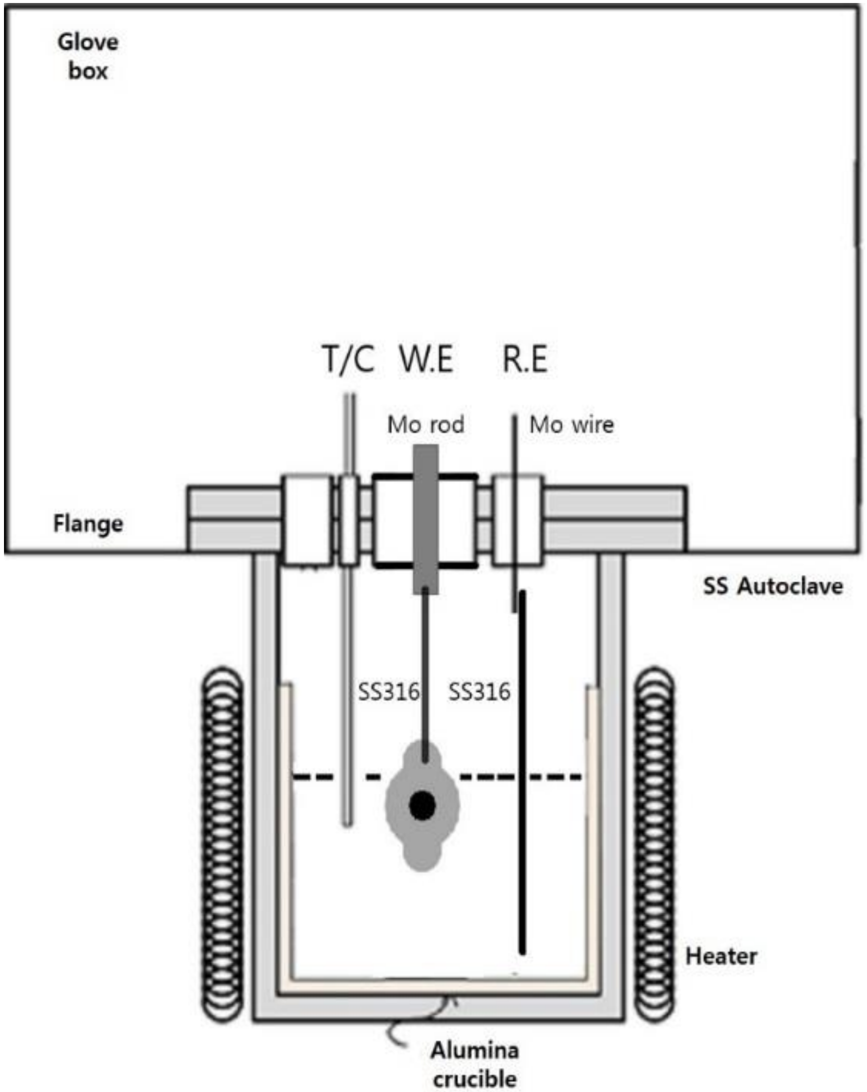
Approach

- Microstructural analysis with
  - ✓Optical Microscope (OM)
  - ✓Scanning Electron Microscopy and attached energy dispersive X-ray spectroscopy (SEM-EDS)
  - ✓Fourier Transform Infrared Spectroscopy (FT-IR)

- Electrochemical analysis with
  - ✓Impedance test

Test Cell


VERSASTAT 3
Compression fitting
(metal with PFTE)
30mm
Cupper gasket
Air
SUS316 wire with electrical
insulation
Test container
Specimen
Alumina crucible
5mm
10mm
Liquid metal (30cc)
54mm
Thermocouple (K-type)
Heater
42mm
48mm

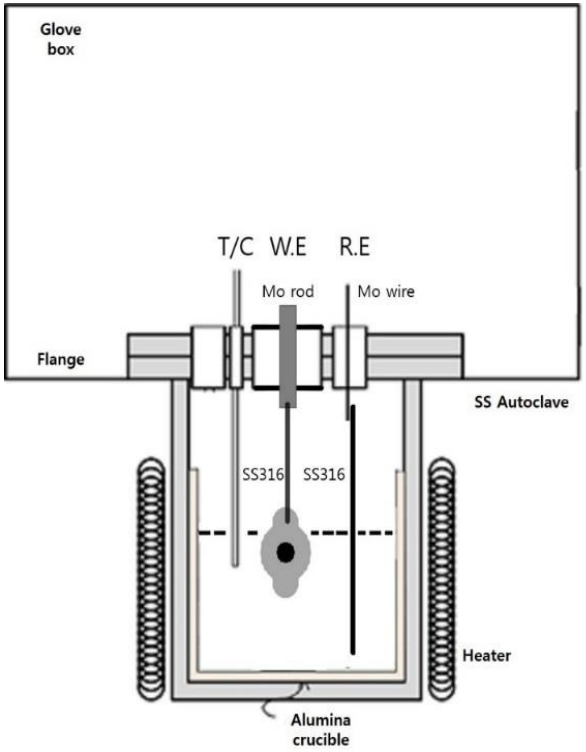

Glove
box
T/C
W.E
R.E
Mo rod
Mo wire
Flange
SS Autoclave
SS316
SS316
Heater
Alumina
crucible

Experiment Condition

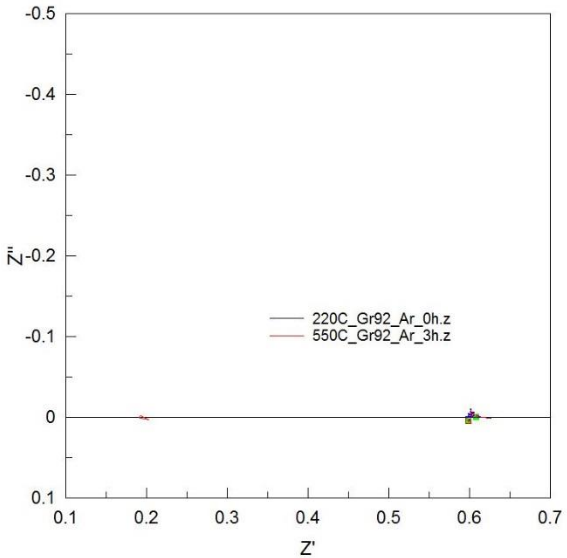
- Materials : Gr92, HT9(Ferrite-Martensite Steel)
- Chemical Composition

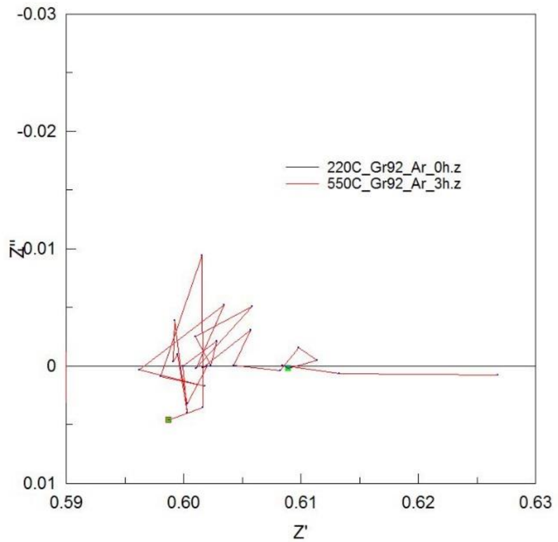
(wt.%)	C	Si	Mn	Cr	Ni	Mo	W	V
Gr92	0.087	0.21	0.41	8.69	0.13	0.38	1.62	0.18
HT9	0.19	0.14	0.49	12.05	0.48	1.00	0.49	0.30

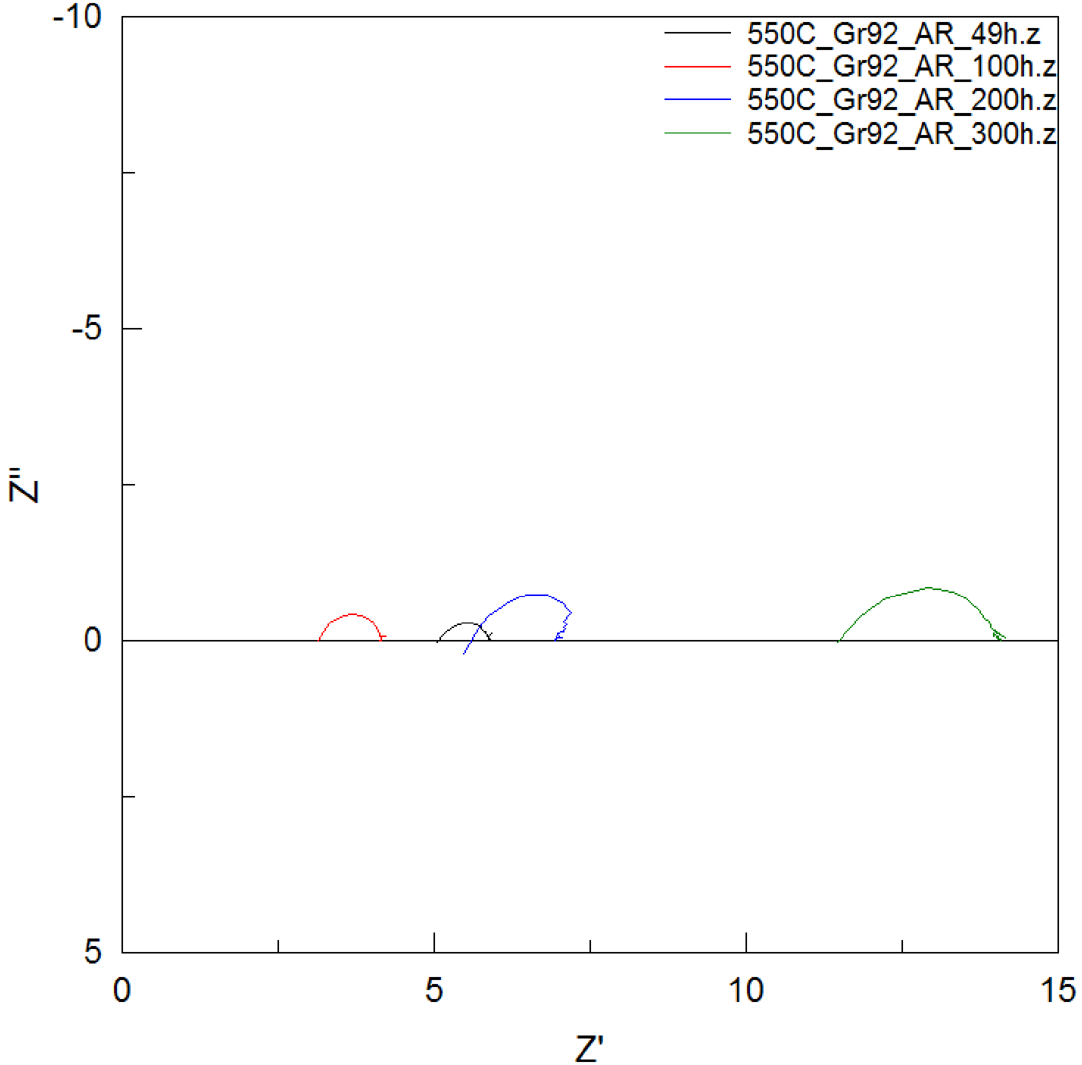
- Applied AC current: 30mV
- Frequency: 0.01Hz~10^7Hz
- Test temperature: 550^{o}C
- Oxygen concentration: Saturated
- Exposure time: 300h



Impedance results of Gr92_AR specimen (Raw)







Impedance results of Gr92_AR specimen

- Figure. 1 is equivalent circuit which represents experiment circuit for electrochemical in liquid sodium.

- From result of impedance data, capacitance of oxide and resistance of oxide can be calculated. Figure. 2 is graph of nyquist plot for result of data and fitting result.

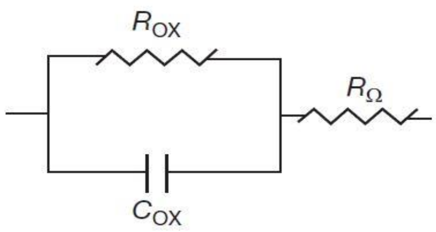


Fig. 1 . Equivalent circuit of an oxide-covered metal in liquid metal where R_{ox} is the resistance of the passive film, C_{ox} is the capacitance of the oxide

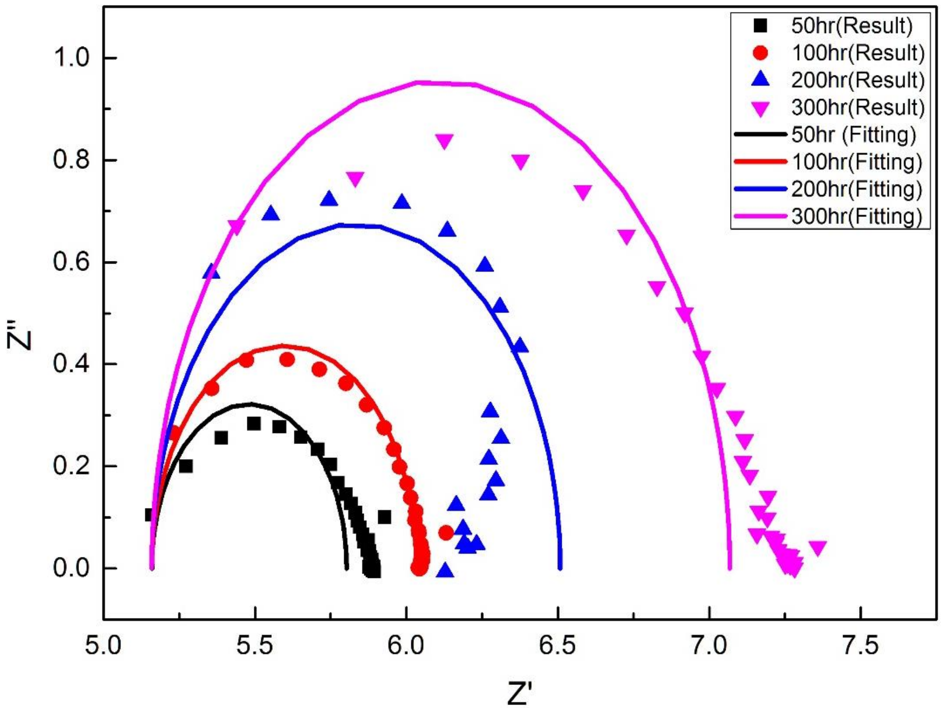


Fig. 2 Result of nyquist plot (dot-result, line-fitting)

Capacitance result and Oxide thickness

Table. 1 Result of capacitance value for time variation

	C
50h	0.00027321
100h	0.00021283
200h	0.00011272
300h	0.00008525

$$d = \frac{\varepsilon \varepsilon_0 S}{C}$$

- where ε is the dielectric constant and ε_0 is vacuum permittivity, S is the electrode area which equals to the surface exposure area of the specimen in sodium, C is capacitance of oxide and d is thickness of oxide.

Table. 2 Result of thickness value for time variation

	C	ε (Assume)	ε_0	S		$\varepsilon * \varepsilon_0 * S$	d (μm)
50h	0.00027321	11	8.854E-12	5.5		5.35667E-10	1.96064
100h	0.00021283	11	8.854E-12	5.5		5.35667E-10	2.51688
200h	0.00011272	11	8.854E-12	5.5		5.35667E-10	4.75236
300h	0.00008525	11	8.854E-12	5.5		5.35667E-10	6.28334

Oxide thickness comparison

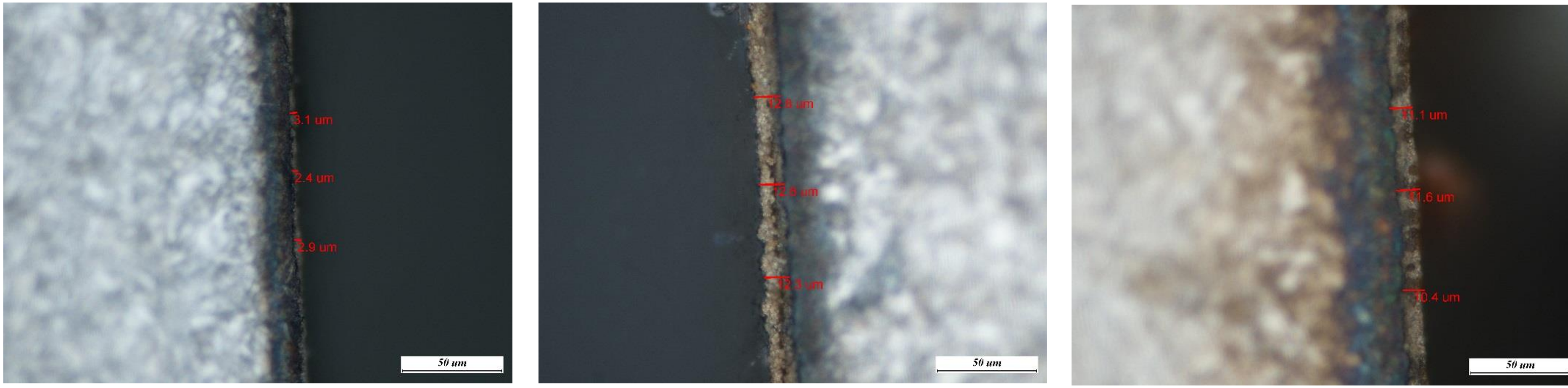


Fig. 1 OM image of Gr92

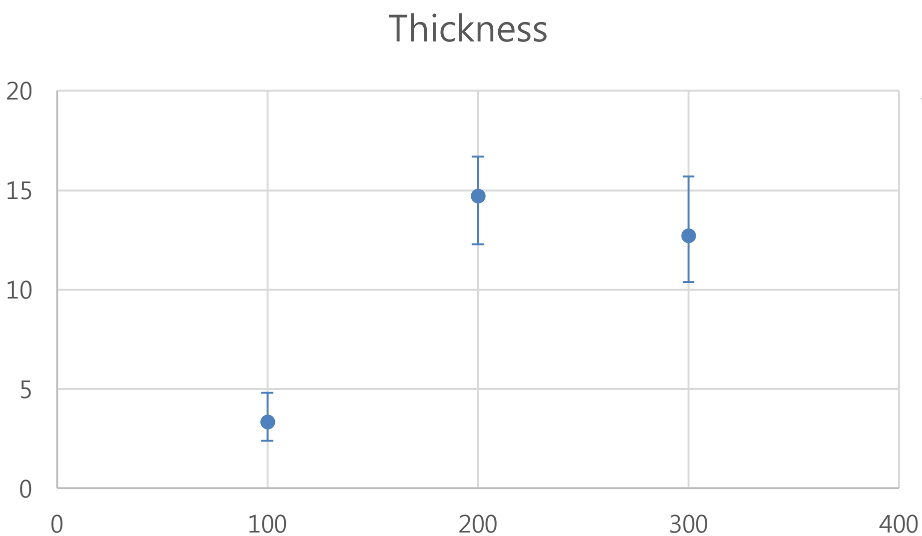


Fig. 2 Result of thickness for Gr92 (OM)

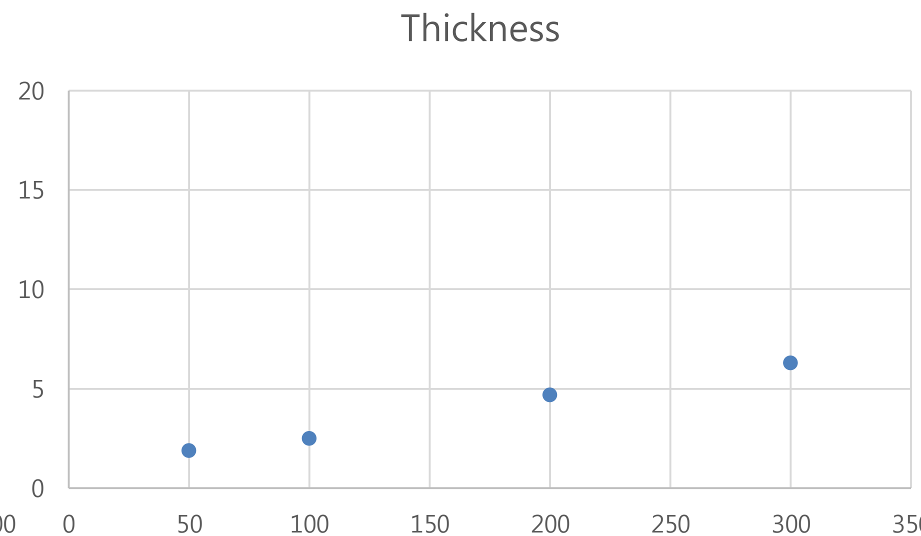


Fig. 3 Result of thickness for Gr92 (EIS)

CVD coating

- SiC and Si_3N_4 Chemical Vapor Deposition (CVD) coating for decarburization barrier on the surface of FMS is considered in this study.
- The CVD coated specimens are experiment for compatibility of high temperature liquid sodium.
- The cross-section images of the SiC and Si_3N_4 coated Gr. 92 and HT9 are shown in Fig. 1. The thickness of coating is 1μm each.

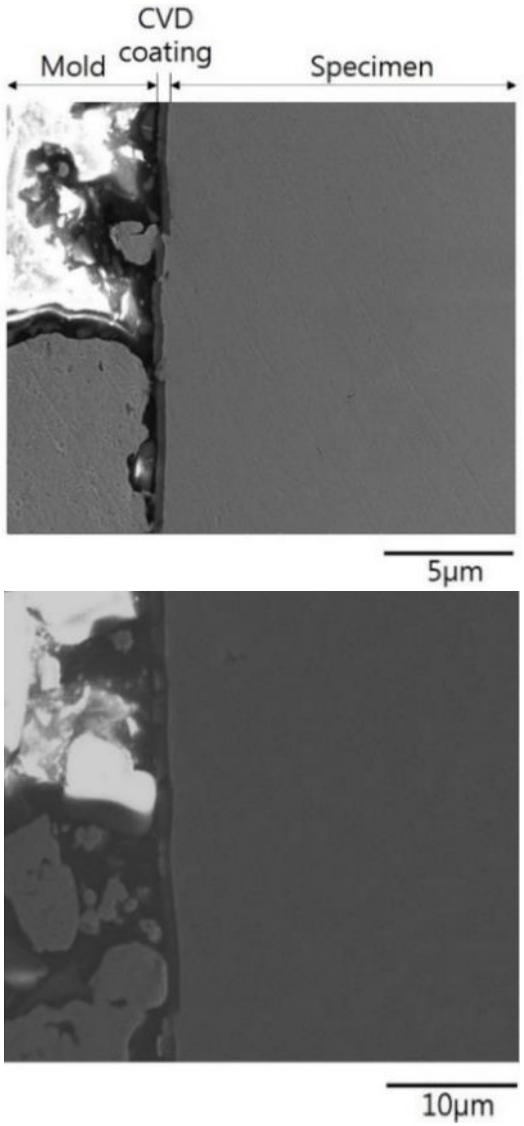


Fig. 1 SEM image of cross section of (a) SiC coating of Gr.92 and (b) Si_3N_4 coating of Gr.92.

Schematic comparison of the oxidation

Aqueous solution environment

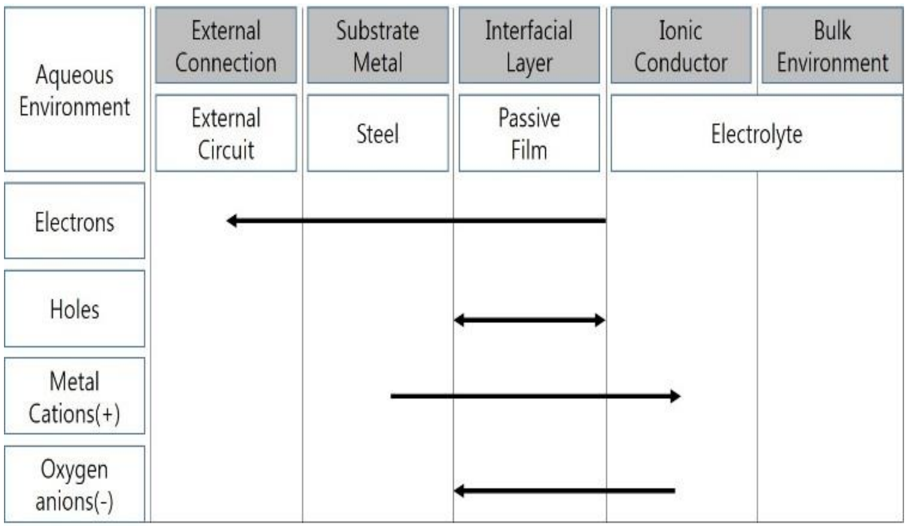


Fig. 1 Aqueous solution oxidation

Liquid sodium environment

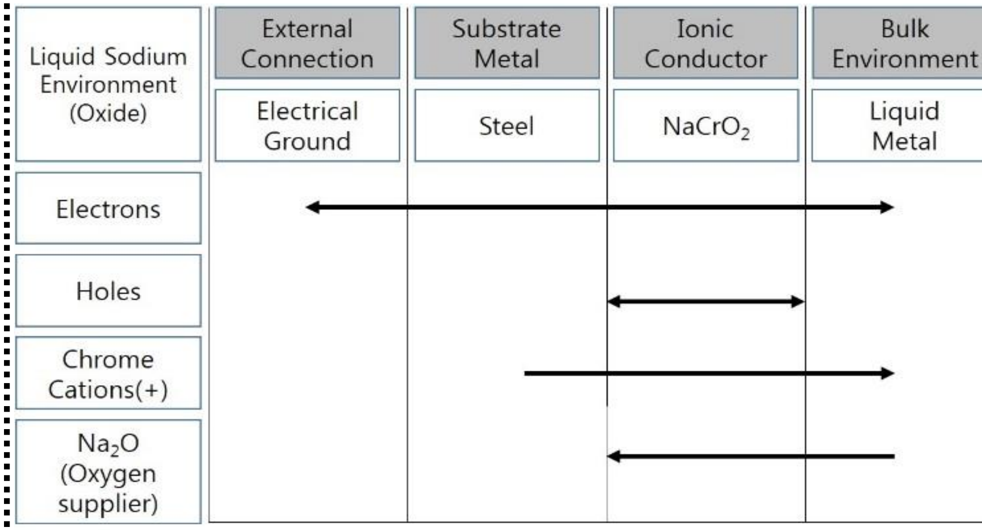


Fig. 2 Liquid sodium oxidation

Dielectric constant of $NaCrO_2$

Table. 1 Result of thickness value for time variation

	C	ε (Assume)	ε_0	S		$\varepsilon * \varepsilon_0 * S$	d
50h	0.00027321	11	8.854E-12	5.5		5.35667E-10	1.96064E-06
100h	0.00021283	11	8.854E-12	5.5		5.35667E-10	2.51688E-06
200h	0.00011272	11	8.854E-12	5.5		5.35667E-10	4.75236E-06
300h	0.00008525	11	8.854E-12	5.5		5.35667E-10	6.28334E-06

- Dielectric constant (ε) is assumed to be 11 value which is Cr_2O_3 of dielectric constant.
- It has to research the similar value for real dielectric constant of $NaCrO_2$.

Oxide thickness comparison

LBE environment

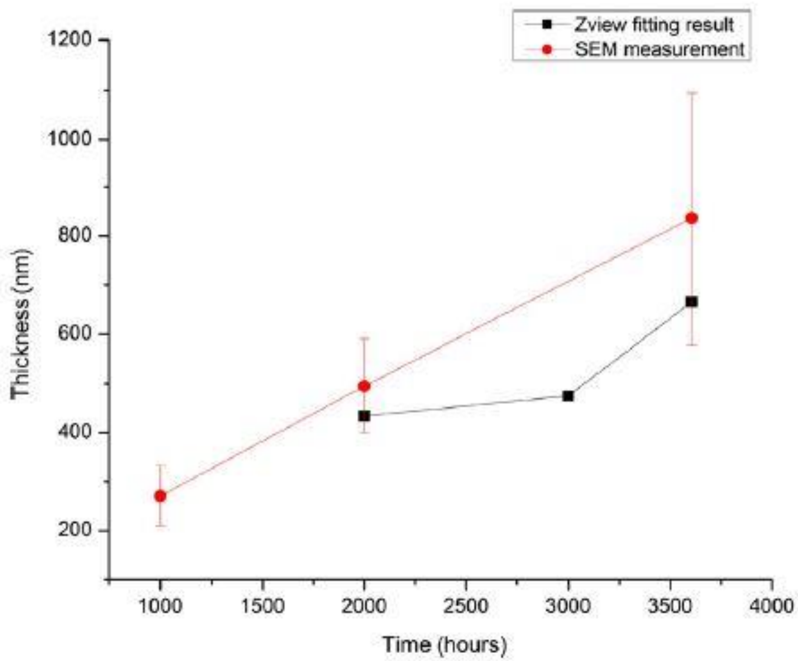


Fig. 1 Comparison of oxide thickness derived from impedance data and SEM measurement

Sodium environment

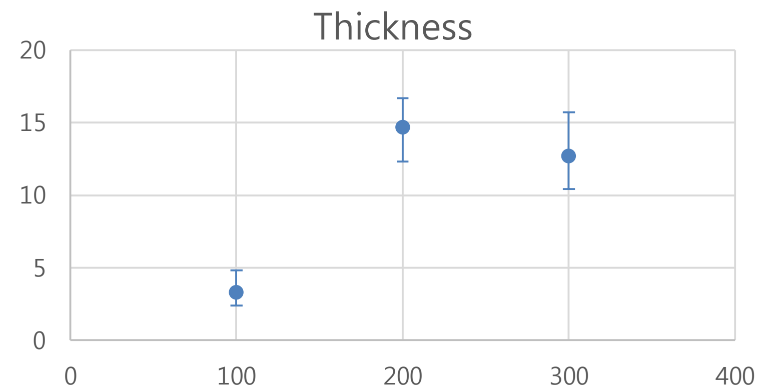


Fig. 2 Oxide thickness for Gr92 from OM measurement

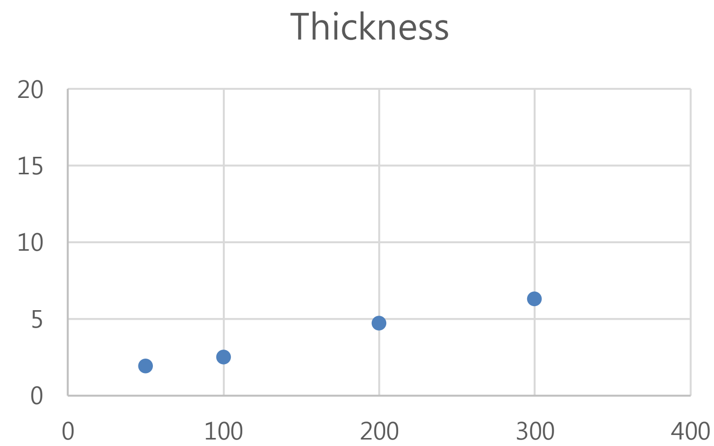


Fig. 3 Oxide thickness derived from impedance

[1] Xiang Chen, Journal of Nuclear Materials 431 (2012) 125.

FT-IR

- The FT-IR data of the PECVD coated specimens is shown in Fig. 1. In the figure. 1 (a), the strong peak at 790cm^{-1} corresponds to the stretching mode Si-C bond, and the weak peaks near 1250, 1800-2000, 3000 cm^{-1} correspond to bending mode Si-CH_3 stretching mode Si-H, and stretching C-H.

- Figure. 1 (b), the strong peak at 900-1000 cm^{-1} corresponds to the stretching mode Si-N bond. From these data, it can be verified that CVD coating well-deposited on surface of specimens.

- The peak of Fig. 1 (a) means SiC existence, and the peak of Fig. 1 (b) means Si_3N_4 existence

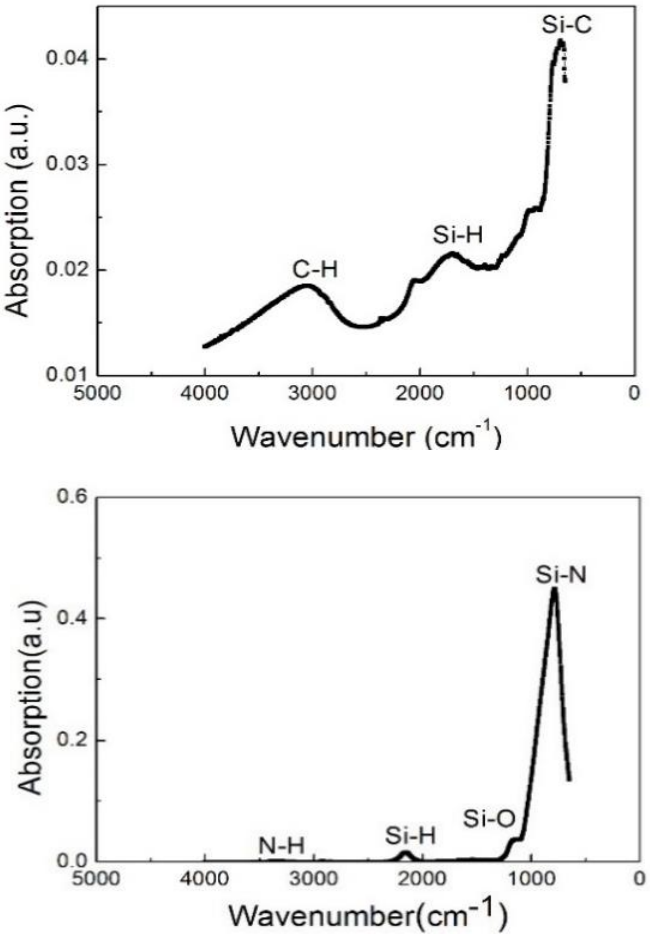


Fig. 1 FT-IR results of CVD Gr.92 (a) SiC coating and (b) Si_3N_4 coating.

Summary

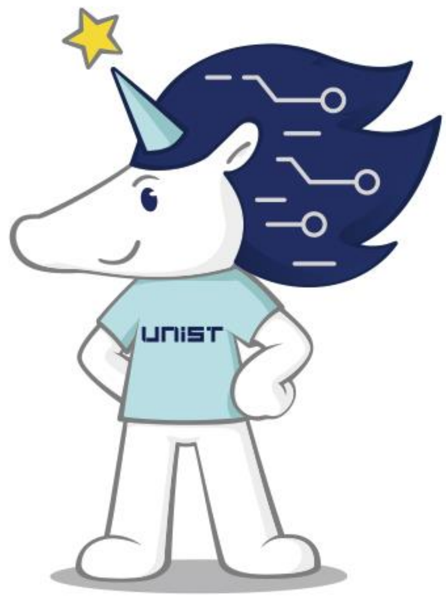
- Summary

✓ Nyquist plot grow up the depend on time.
✓ EIS result comes from the oxide layer.
✓ EIS result can verify the oxide thickness growth.
✓ By comparing OM image, EIS data can verify the meaningful results.
✓ The CVD coating is deposited on surface of FMS well. The peak of 790cm^{-1} corresponds to the stretching mode Si-C bond, and 900-1000 cm^{-1} corresponds to the stretching mode Si-N bond.

- Future Plan

✓ Research the dielectric constant of $NaCrO_2$.
✓ Experiment to the HT9 experiment.
✓ The CVD coated specimens will be tested on same experiment environment which is 550°C liquid sodium for 0 to 300 hour exposure time.
✓ Oxide films($NaCrO_2$) effect to FMS material.

Thank you for your attention!



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