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

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INTRODUCTION

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. The compatibility of cladding and structural materials with sodium has to be carefully investigated, as sodium could promote corrosion of cladding and structural materials in two ways. One is produced by the dissolution of alloy constituents into the sodium, and the other is produced through a chemical reaction with impurities (especially oxygen and carbon) in the sodium environment [1].

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 [2]. So, it is very important to investigate the corrosion-related behavior such as surface corrosion rate, carburization, decarburization and mechanical properties for its operation time.

The decarburization process where dissolved carbon near the specimen surface diffused in to the liquid sodium. This process can originate from the difference between dissolved carbon activity in the material and liquid sodium. A compatibility test the cladding tube revealed that a decrease of the mechanical property instigated by the aging proves governed the whole mechanical property [3].

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.

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. The use of the technique of impedance spectroscopy to measure the electrical impedance response of any oxide layers, SiC and Si_3N_4 that may be present may be a solution to this monitoring problem.

METHODOLOTY

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It is known that sodium promotes corrosion in two ways. One is corrosion produced by dissolution of alloy elements into sodium, and the other is corrosion produced through a chemical reaction with the impurities in sodium (especially dissolved oxygen).

In the Hémery paper, $NaCrO_2$ is formed on T91 steel surface in liquid sodium at 723K for 48h. Though low oxygen concentration (10 $x10^{-4}$ atomic %) dissolved in liquid sodium, oxides can be formed on the T91 (9Cr-1Mo steel) [4]. In this study, we research the corrosion behavior especially oxidation at the surface on materials in liquid sodium environment. The EIS method can monitor the corrosion behavior observed at the surface of the materials by in-situ.

In the Lillard paper, EIS has also been applied to investigate oxide on metals in sodium (Na)-cooled and Lead-Bismuth Eutectic (LBE) cooled systems that simulate reactor environments. The equivalent circuit (EC) used to model the data is similar to the simplified Randles circuit; however, in this case, there is no electrochemical double layer, only the impedance and capacitance associated with the oxide as shown Fig. 1. In this EC, R_{ox} is the direct current resistance of the oxide, C_{ox} is the oxide capacitance and R_Ω is the geometric resistance associated with the liquid metal (Na or LBE) [5]. So, EIS experiment can be verified the oxide existence for as-received specimen surface.
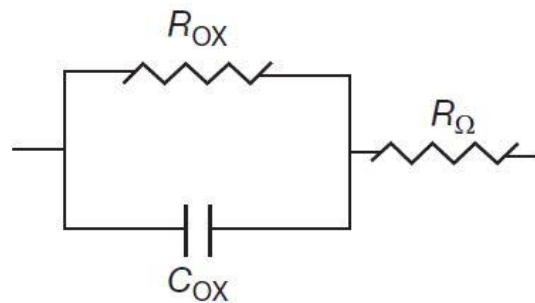

Fig. 1. Equivalent circuit of an oxide-covered metal in liquid metal where R_{ox} is the resistance of the passive film, C_{ox} is the capacitance of the oxide [6].

In the corrosion of a pure metal by sodium, the solid is dissolved in the liquid in elemental form at a rate that

depends on the speed of two consecutive steps: (1) Release of metal atoms from the surface to the liquid sodium immediately adjacent to the solid. (2) Transport of the dissolved metal through the liquid boundary layer attached to the solid. From these steps, it is proceeding corrosion behavior which is carbon migration and oxide formation.

Oxygen dissolves in sodium as the monoxide Na_2O. Assuming compound formation, we may commence by considering the reaction (Equation [1]). In the liquid sodium environment, $NaCrO_2$ is more stable compound than Na_2O as shown Fig. 2. Na_2O encounter electrons, then it forms the NaO_2^{3-} and Na (Equation [2]). And chrome atom emits the electron which is cation (Equation [3]).
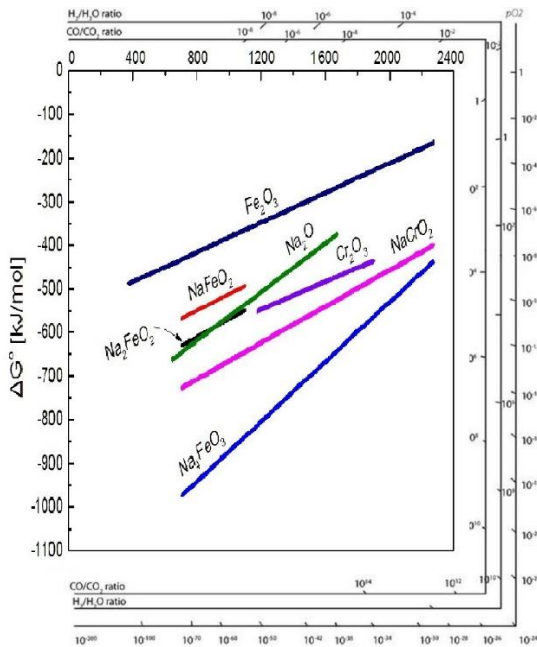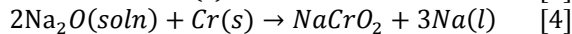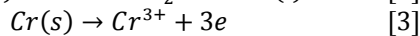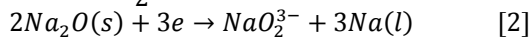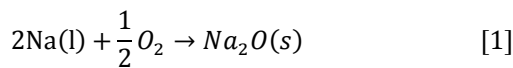

Fig. 2. Ellingham diagram in liquid sodium environment.

And chromium is a strong oxide former, and sodium chromite, $NaCrO_2$, forms readily according to the reaction (Equation [4]). The reaction has been written for Na_2O in solution in sodium. This oxide can confirm by EIS [6].

$$2Na(l) + \frac{1}{2}O_2 \rightarrow Na_2O(s) \qquad [1]$$
$$2Na_2O(s) + 3e \rightarrow NaO_2^{3-} + 3Na(l) \qquad [2]$$
$$Cr(s) \rightarrow Cr^{3+} + 3e \qquad [3]$$
$$2Na_2O(soln) + Cr(s) \rightarrow NaCrO_2 + 3Na(l) \qquad [4]$$

The electrochemical which liquid metal environment has different mechanism from aqueous solution environment Fig. 3. In the aqueous solution environment, role of electrolyte is electron transport mediator. In the liquid metal environment, however, role of liquid metal is not electron transport mediator and role of electrode. And, oxide play a role as ionic conductor [7].

Films of SiC and Si_3N_4 are typically grown on low-temperature substrates by plasma-enhanced chemical vapor deposition (PECVD). In this study, CVD coated films grown by PECVD are analyzed by Fourier Transform Infrared Spectroscopy (FT-IR) to elucidate the hydrogen content of the films based on the bonding scheme determined from the peak shift in the spectra. From the FT-IR spectra of the film, the integrated absorption intensity of the stretching mode of Si-H and C-H bonds was calculated. And the PECVD coated specimen can be measured by EIS as shown in Fig. 3 (c). Ceramic also capacitance and R_Ω is the geometric resistance associated with the liquid sodium environment.
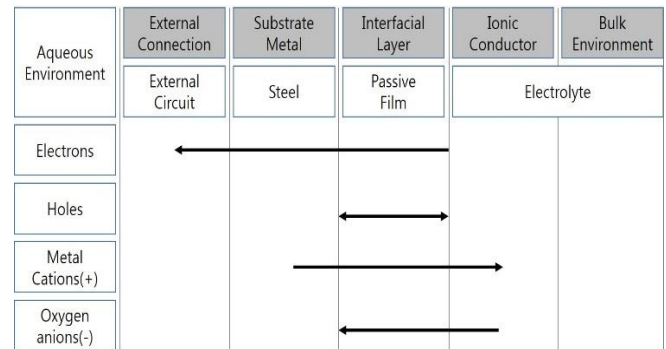
(a)
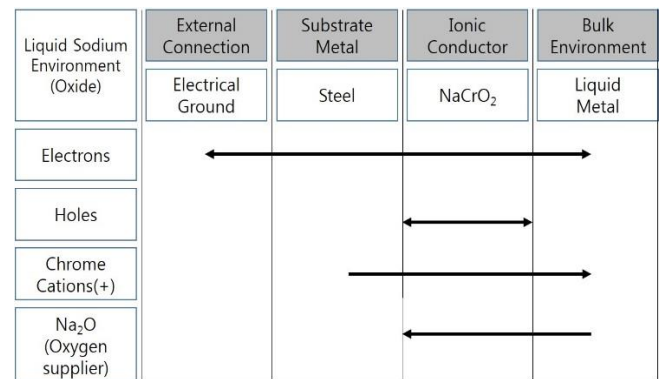
(b)
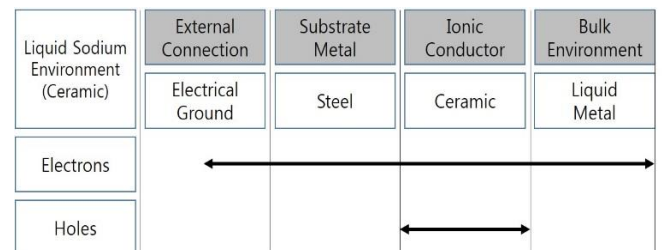
(c)

Fig. 3. Schematic comparison of the parts and (a) processes involved in aqueous [6] and (b) liquid sodium oxidation and (c) electrons movement in liquid sodium.
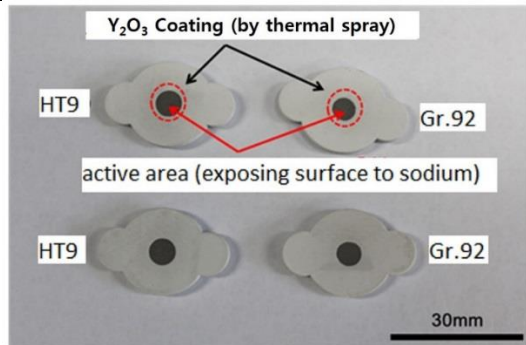
EXPERIMENT

The surface of FMS steel is working electrode. And, the SS316 wire was role of reference electrode because SS316 is stable material in liquid sodium.

Liquid sodium is located at stainless steel autoclave in glove box. Dissolved oxygen is saturated in liquid sodium.
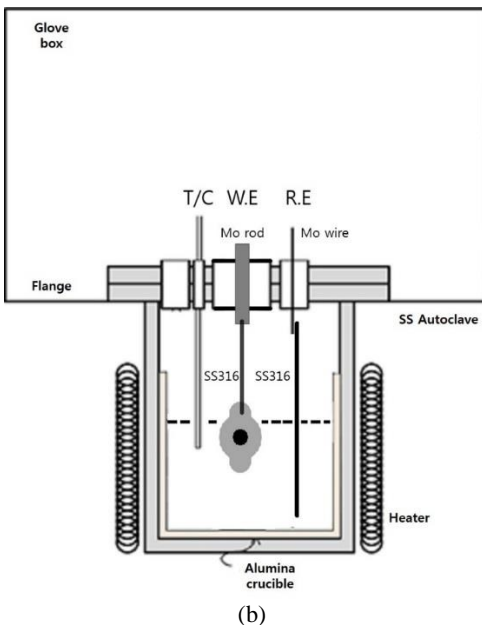
The chemical composition of FMS test materials is shown in Table. 1. Specimen of Gr.92 and HT9 was coated by thermal spraying method with about 90-100 μm thickness of Y_2O_3 except the active area as shown in Fig. 4 (a).

Table 1. Chemical composition of the test material

	C	Si	Mn	Cr	Ni	Mo	W	V
Gr.92	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

(a)

(b)

Fig. 4. Electrochemical Impedance Spectroscopy (EIS) test preparation with (a) coated working electrode (Gr.92 and HT9) and (b) experimental set up.

RESULTS

Before exposure to sodium, some specimens were CVD coating process which was SiC and Si_3N_4 coating. The cross-section images of the SiC and Si_3N_4 coated Gr. 92 and HT9 are shown in Fig. 5. The thickness of coating is 1μm each.

The FT-IR data of the PECVD coated specimens is shown in Fig. 6. In the Fig. 6 (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. The Fig. 6 (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. 6 (a) mean SiC existence, and the peak of Fig. 6 (b) mean Si_3N_4 existence

CONCLUSIONS

In the liquid sodium environment, chemical reaction can formation the oxide layer. The mechanism of electrochemical impedance spectroscopy is different from liquid metal environment and general environment like aqueous environment. EIS has been applied to investigate passive oxide layer on metals in sodium system. Also, CVD coated layer can be confirmed the existence in liquid sodium by EIS.

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 WORK

The EIS tests at higher temperature with as-received HT9 and Gr.92 specimens are under process and also as-received specimens were exposed to oxygen saturated sodium environment for $NaCrO_2$ formation on the surface for further EIS tests.

The CVD coated specimens will be tested on same experiment environment which is 550°C liquid sodium for 0 to 300 hour exposure time. The Silicon Carbide (SiC) coating and Silicon Nitride (Si_3N_4) coating specimen will be exposed to oxygen saturated sodium environment. After exposure process, role of SiC and Si_3N_4 can be analyzed, and difference from corrosion behavior on non-deposition specimen to deposition specimen can be analyzed. The CVD coating can play role of protection film for oxidation and decarburization.
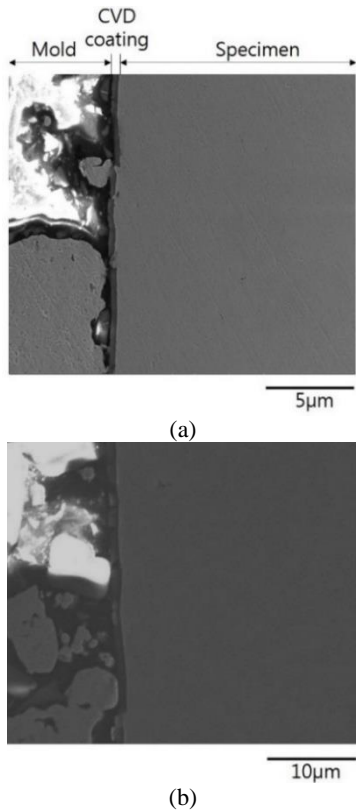
(a)

(b)

Fig. 5. SEM image of cross section of (a) SiC coating of Gr.92 and (b) Si_3N_4 coating of Gr.92.

(a)

(b)

Fig. 6. FT-IR results of CVD Gr.92 (a) SiC coating and (b) Si_3N_4 coating.

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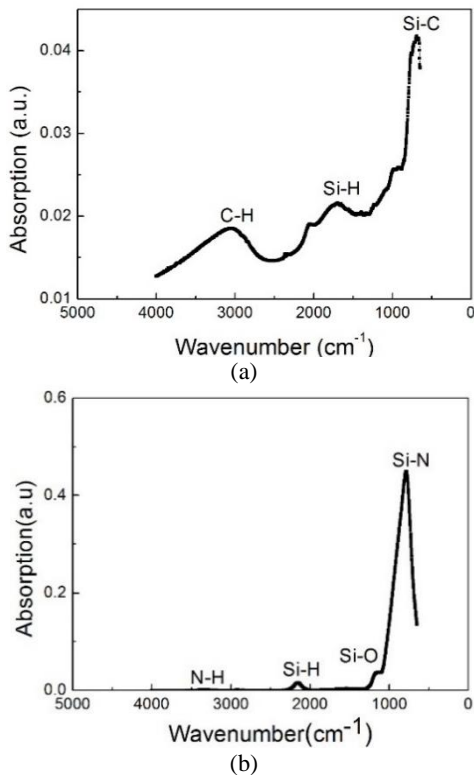7. J.F. Stubbins, A. M. Bolind, X. Chen, J. Nucl. Mater. 337, 243 (2008).