Feasibility Study on Nano-structured Coatings to Mitigate Flow-accelerated Corrosion in Secondary System of Nuclear Power Plants

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1. Introduction

Carbon steel is widely used as a structural material in intensive energy generating systems, especially piping elements for secondary system of nuclear power plants. However it is generally known that the passivity of carbon steel is not sufficient for protection in harsh environments with the presence of aggressive atoms because of the continuous dissolution of ferrous and magnetite ions so called flow-accelerated corrosion (FAC).

There have been many efforts to mitigate FAC [1] through the adoption of the advanced and modified water chemistries such as optimized dissolved oxygen (DO) concentration and temperature. However, these mitigation techniques pose certain challenges relating to the compatibility of new water chemistries with the steam generator, the thermal efficiency of the secondary side, etc. In this context, nano-particle reinforced electroless nickel plating (NP ENP) could help solve the FAC issues in secondary pipe systems. This does not require modification of water chemistry or structural materials, and hence, its application is reasonable and time-saving compared to previous FAC mitigation techniques.

The main parameters of FAC are known as electrochemical reaction at the interface, dissolution of magnetite and ferrous ions due to concentration gradient between carbon steels and water and wear due to a fast-flowing fluid. Nano-particles, such as TiO_2, SiC, Al_2O_3, WC and ZrO_2 in the nickel coating layer help decrease the corrosion current in aggressive environments [2-6] compared coatings without nano-particles, and also improve the mechanical properties especially hardness, through precipitations. Also, the addition of nano-particles reduces the grain size of nickel resulting in low surface roughness because nano-particles provide nucleation sites for nickel during plating process. In other words, NP ENPs have the potential to mitigate FAC in the secondary systems.

Even though the advantages of NP ENPs in engineering and industrial applications, their corrosion characteristics in high-temperature and feasibility study in secondary water chemistry were not researched enough. Therefore in this study, the feasibility of NP ENP especially $Ni-P-TiO_2$ and Ni-P-SiC is investigated in order to reduce or mitigate the FAC of carbon steel in the simulated secondary system of nuclear power plants.

2. Methods and Results

In this section preparation of coatings and methods for high-temperature electrochemical experiments and FAC simulation experiments were described.

2.1 Preparation of Coatings

For the NP ENPs, SA516 Gr.60 carbon steel samples of size $20 \times 20 \times 5$ (mm) were prepared. Prior to electroless nickel plating, the samples were mechanically polished with #400, #600 and #800 SiC papers and cleaned using a detergent and rinsed with water and acetone and then alkaline cleaned in 10 vol% of NaOH for 5 min in 25 °C and rinsed with deionized water in ultrasonic bath. For the activation of surface, samples were immersed in 8 vol.% H_2SO_4 solution for 10 sec then rinsed with deionized water. To avoid the corrosion of the samples in air, the samples were immersed in the nickel plating bath immediately.

Before the plating processes, the prepared baths are stirred using magnetic stirrer in 300 RPM for 1 hr and heated up to 80 °C in ultrasonic bath. $NiSO_4 \cdot 6H_2O$, $NaH_2PO_2 \cdot H_2O$, $Na_3C_6H_5O_7 \cdot 2H_2O$, H_2NCH_2COOH, $(NH_4)_2SO_4$ were used as a nickel source, reducing agent and complexing agent, brightening agent and pH buffer, respectively. Bath A does not contain any nano-particles and surfactant and the bath B and C contains 2 g/L of TiO_2 and SiC nano-particles and for their agitation in the nickel baths and nickel plating layer, $NaC_{12}H_{25}SO_4$ (sodium dodecyl sulfate; SDS) was added in each nickel baths. SDS is an anionic surfactant which inducing negative zeta potential to TiO_2 and SiC nano-particles in a solution so pH was adjusted to 9 because the zeta potential of TiO_2 nano-particles is negative in alkaline baths. Small amount of NaOH solution were used to adjust pH of the nickel baths. The temperature of all baths were kept in 80 °C and stirred in 200 RPM using magnetic stirrer. The plated samples were rinsed with deionized water and ultrasonically cleaned to remove remaining chemicals and nano-particles then the samples were heat-treated in a furnace of 400 °C with argon atmosphere for 1 hr. The changes between as-plated and heat-treated samples
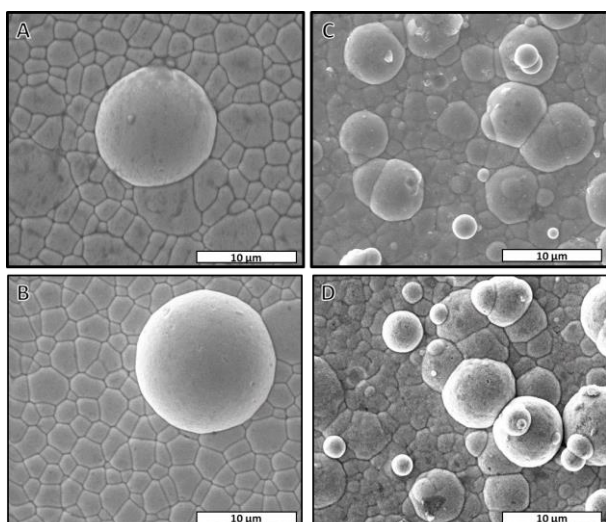
Fig. 1. SEM images of surface of (A) as-plated Ni-P, (B) heat-treated Ni-P, (C) as-plated Ni-P-TiO$_2$ and (D) heat-treated Ni-P-TiO$_2$ samples.
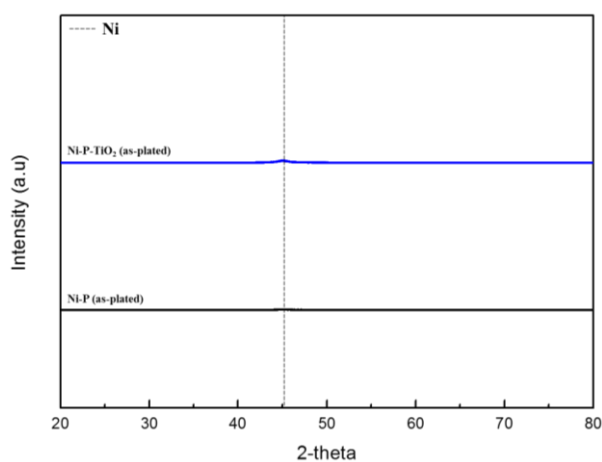

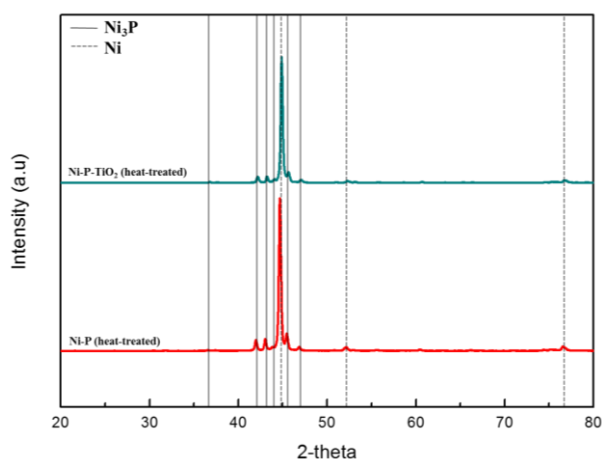Fig. 2. XRD peaks prior to heat-treatment for Ni-P and Ni-P-TiO$_2$

Fig. 3. XRD peaks after to heat-treatment for Ni-P and Ni-P-TiO$_2$

were carried out using high-power X-ray diffractometer (XRD) (D/MAZX 2500V/PC, Rigaku, Japan).

The surface morphologies of Ni-P and Ni-P-TiO$_2$ prior to and after heat-treatment indicate the presence of TiO2 nano-particles in the plating bath leads to the formation of nickel nuclei on the surface because the nano-particles provides nucleation sites for nickel ions like Fig. 1. However, the heat-treatment does not make effects on the surface morphologies but the formation crystalline phase especially Ni$_3$P. Ni$_3$P phase is an precipitation for nickel matrix and induces the improved mechanical properties and corrosion resistance.

2.2 High-temperature Electrochemical Experiments

In this study, high-temperature corrosion characteristics of NP ENPs in 150 °C ETA electrolytes were investigated by open circuit potential (OCP), potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) measurements using PAR 273A Potentiostat (Princeton Applied Research, US) and Solartron 1260A Impedance Analyzer (Solartron Analytical, US).

As electrolyte, 9 ppm ethanolamine (ETA) solution was prepared using deionized water and measured pH was 9.3±0.2 which is similar to typical secondary water chemistry of nuclear power plants. The electrolyte was fully purged using high purity (99.999%) argon gas until DO kept less than 10 ppb.

The results of high-temperature electrochemical experiments were listed in Fig. 4., Fig. 5., Table I and Table II. From the results, it is determined that both Ni-P and Ni-P-TiO$_2$ can be effective corrosion barrier for secondary water chemistry. The addition of the nano-particles induces the shift of polarization curves to nobler region with more negative corrosion potential. Nyquist plots indicate the formation of bi-layer at the surface. The corrosion model based on EIS results will be established in the near future.

2.3 FAC Simulation Experiments

The FAC simulation experiments will be carried out in secondary water chemistry control system and magnedrive-installed autoclave which can simulates 4 m/s flow velocity as maximum. The coated samples will be installed in the autoclave and their surface and cross-section morphologies will be analyzed and their weight loss and thickness change will be measured.

3. Conclusions

- For the application in secondary system, Ni-P and Ni-P-TiO$_2$ coatings were prepared
- High-temperature corrosion characteristics of the both coatings have potential as FAC barrier for carbon steel
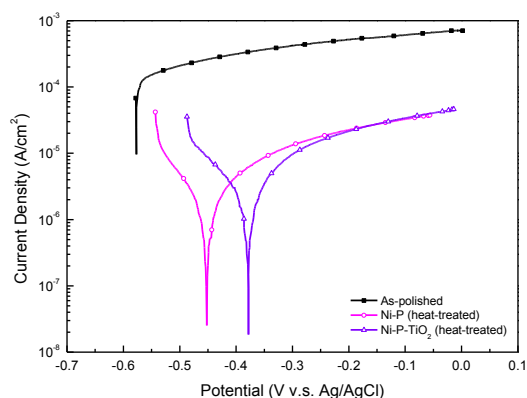- Feasibility study will be carried out with FAC simulation experiments

Fig. 4. Potenitodynamic polarization curves of as-polished, Ni-P (heat-treated), Ni-P-TiO$_2$ (heat-treated) samples in 150 $^\circ$C ETA solution.

Table I: Fitting parameters for electropolarization curves

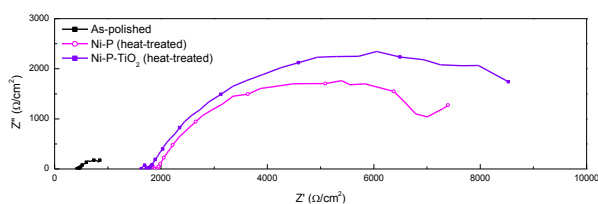|	As-polished	Ni-P	Ni-P-TiO$_2$
R_P (Ω/cm^2)	141	8578	11036
I_0 (A/cm^2)	1.84×10^{-4}	3.04×10^{-6}	2.35×10^{-6}
E_0 (V)	-0.581	-0.378	-0.451

Fig. 5. Nyquist plots of as-polished, Ni-P (heat-treated), Ni-P-TiO$_2$ (heat-treated) samples in 150 $^\circ$C ETA solution.

Table II: Fitting parameters for Nyquist plots

	As-polished	Ni-P	Ni-P-TiO$_2$
R_s (Ω/cm^2)	429.5	1750	1626
R_p (Ω/cm^2)	23.98	168.8	149.4
C_{dl} (F/cm^2)	4.70×10^{-7}	7.39×10^{-8}	6.82×10^{-8}
n_{inner}	0.897	0.900	0.870
R_p (Ω/cm^2)	587.4	6084	8139
C_{dl} (F/cm^2)	3.87×10^{-4}	3.83×10^{-6}	4.59×10^{-7}
n_{inner}	0.661	0.676	0.667

4. Acknowledgement

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