

Application of Nano-Structured Coatings for Mitigation of Flow-Accelerated Corrosion in Secondary Pipe Systems of Nuclear Power Plants

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1. Introduction

Flow-accelerated corrosion (FAC) is a corrosion process in which a normally protective oxide layer on a surface dissolves in a fast flowing water. In other words, FAC is a complex corrosion process combined with mechanical reaction with fluid.

There were lots of research to mitigate FAC such as controlling temperature or water chemistry but in this research, we adopt active coating techniques especially nano-particle reinforced coatings.

One of the general characteristics of FAC and its mitigation is that surface friction due to surface morphology makes a significant effect on FAC [1]. Therefore to form a uniform coating layers, nano-particles including TiO₂, SiC, Fe-Cr-W and Graphene were utilized[2-6]. Those materials are known as greatly improve the corrosion resistance of substrates such as carbon steels but their effects on mitigation of FAC are not revealed clearly.

Therefore in this research, the FAC resistive performance of nano-structured coatings were tested by electrochemical impedance spectroscopy (EIS) in room temperature 15 wt% sulfuric acid.

2. Methods and Results

In this section, the procedures for the each coatings and electrochemical experiments were introduced. Additionally, surface and cross sectional morphologies observation and electrochemical analysis are introduced.

2.1 Sample Preparation

The structural material for secondary piping system is carbon steels including A106 Gr.B and A516 Gr.60. There are chemical composition for each materials are described in Table I.

Table I. Chemical composition for carbon steels

	A106 Gr.B	A516 Gr.60
C	0.28 Max	0.21 Max
Si	0.1 Min	0.15 – 0.4
Mn	0.29 – 1.18	0.6 – 1.2
P	0.03 Max	0.035 Max
S	0.03 Max	0.035 Max

Cu	0.4 Max	0.006
Ni	0.4 Max	0.01

For this experiments, A516 Gr.60 were prepared because A106 Gr.B does not provide plate time sample. Sample geometry is 40*20*5(mm) and before coating procedures, surfaces are polished with SiC papers of 320 grit and cleaned with detergent, ethanol and acetone. Then supersonic cleaned in distilled water for 10 mins.

2.2 Coating Procedures

As candidate coatings for FAC mitigation, TiO₂ and SiC reinforced electroless nickel plating, Fe-Cr-W HVOF spray and grapheme were prepared.

For TiO₂ and SiC reinforced electroless nickel plating, TiO₂ (Sigma Aldrich, 21 nm, 718467) and SiC (Sigma Aldrich, <100 nm 594911) nano powders were prepared.

For electroless nickel plating, standard Watt's bath were prepared and the nanoparticles were injected with suitable surfactants. Table II is the quantities for chemicals and coating parameters.

Table II. Electroless nickel plating bath composition

	Quantity
NiSO₄	15 g/L
NaH₂PO₂	14 g/L
NaCH₃COO	13 g/L
HF(40%)	12 ml/L
NH₄HF₂	8 g/L
Thiourea	1 mg/L
TiO₂, SiC	12 g/L

For Fe-Cr-W HVOF spraying, SHS7740TM nano powder were prepared. The surfaces were coated with SHS7740TM and to remove porosity, Densifier 500 and Densifier 1500 were coated on the surfaces.

2.3 Surface Morphologies

Surface and cross section morphologies of each samples were observed with scanning electron microscope(SEM) with 10.0 kV.

Figure 1 is the observed surface morphologies for each samples. A is Ni-P electroless nickel plating, B is Ni-P-TiO₂ electroless nickel plating, C is SHS7740

with Densifier 500 and D is SHS7740 with Densifier 1500.

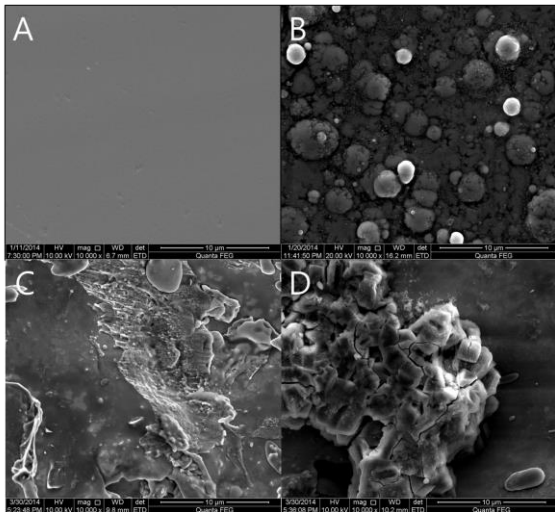


Fig. 1. Surface morphologies of coated samples. (A) Ni-P electroless nickel plated, (B) Ni-P-TiO₂ electroless nickel plated, (C) SHS7740 with Densifier 500 and (D) SHS7740 with Densifier 1500.

From the Fig.1 (A) shows that electroless nickel plating provides completely clean and uniform surface on a substrate. However, compared to (A), TiO₂ reinforced electroless nickel plating (B) shows ball shape surface, the growth of nickel on the TiO₂ nano powder. However, nano-structure is not formed because of dispersion. Therefore, suitable surfactant should be added to Watt's bath and sodium dodecyl sulfate (SDS) will be added. (C), (D) is an HVOF sprayed Fe-Cr-W nano powder with different densifier. Densifier effects are not revealed in this surface morphologies so cross sectional morphologies are also observed with SEM.

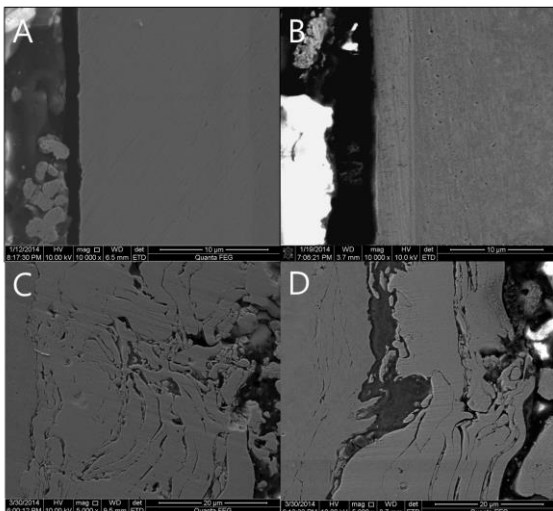


Fig. 2. Surface morphologies of coated samples. (A) Ni-P electroless nickel plated, (B) Ni-P-TiO₂ electroless nickel plated, (C) SHS7740 with Densifier 500 and (D) SHS7740 with Densifier 1500.

Cross section morphologies of Ni-P (A) and Ni-P-TiO₂ (B) shows the uniform coating layers on substrates compared to SHS7740 (C, D). Coating thickness of nickel plating coatings were 15 – 20 μm with nickel strike plating layer at the interface between Ni-P layers and substrates.

SHS7740 HVOF spray does not shows the formation of uniform coating layers. Densifier 500 does not shows the removal of porosity but Densifier 1500 reveals the removal of the porosity at the insider of coating layers. Therefore, for the mitigation of FAC and reducing surface friction of SHS7740, grinding of surface should be introduced.

2.4 Electrochemical Analysis

To test corrosion mitigation properties for each samples, electrochemical cell and potentiostat PAR 273A were prepared. Electrolyte is nitrogen purged 15 wt% sulfuric acid and reference electrode is saturated calomel electrode (SCE, 0.241 V vs NHE). Platinum mesh counter electrode is installed in the cell. Surface area of working electrode is 0.785 cm².

Electropolarization measurements were conducted in the range of -1.5 V ~ 1.5 V versus open circuit potential(OCP) with the scan rate of 50 mV/sec. Impedance spectroscopy were conducted at 0 V versus OCP and AC amplitude is 10 mV. Frequency is in the range of 10⁻² to 10⁶.

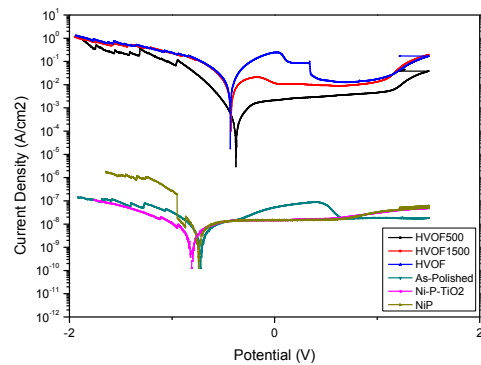


Fig. 3. Electropolarization curves for nano-structured coating samples.

The results of electropolarization curves are revealed in Fig. 3. To qualify reproducibility, there were three tests for each samples. It is visualized that, electroless nickel plated samples including the TiO₂ reinforced samples shows slightly lower value of potential (E_0) compared to SHS7740 samples. This means that Fe-Cr-W nano powders are susceptible to 15 wt% sulfuric acid environments.

Also, current density at E_0 (I_0) is 10⁶ times higher for SHS7740 samples which reinforces the result of potential shift.

Densifiers for SHS7740 reinforces the passivity of substrates and coating layers at the range of -0.3V to

1.0V and there are similar phenomenon electroless nickel plated samples compared to as-polished samples.

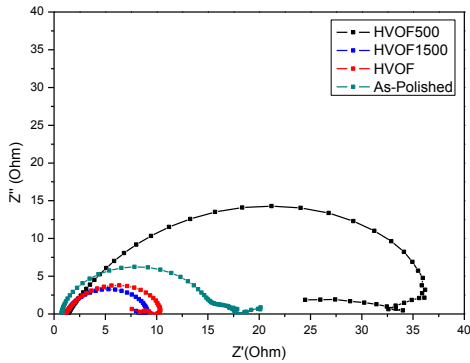


Fig. 4. Nyquist complex plots for SHS7740 with Densifier 500, 1500 and as-polished samples

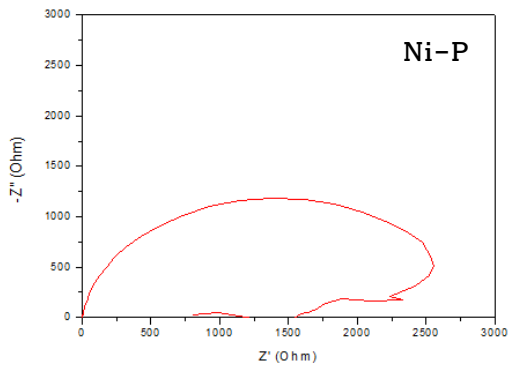


Fig. 5. Nyquist complex plots Ni-P electroless nickel plated sample

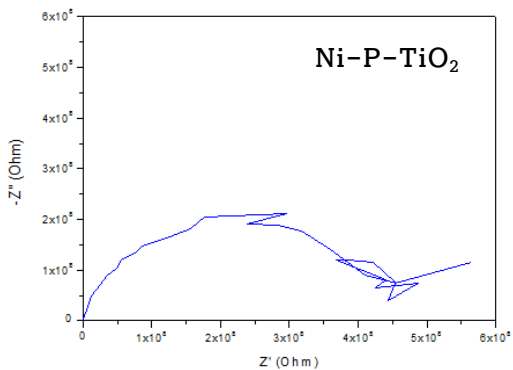


Fig. 6. Nyquist complex plots for SHS7740 with densifier 500, 1500 and as-polished samples

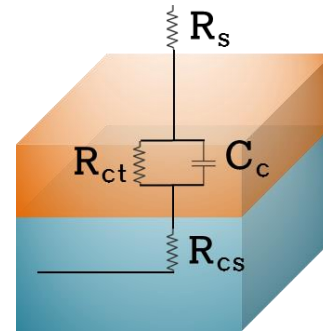


Fig. 7. Equivalent circuit model for coating samples

From the Nyquist complex plots, the resistance and capacitance for electrolyte, coating layers and substrates are measured by constructing equivalent circuits.

From Fig. 4., the resistance of electrolyte (15 wt% sulfuric acid) is measured as 2.5 Ω . The charge transfer resistance (R_{ct}) for as-polished, HVOF500, HVOF1500 and HVOF without Densifier are 17.5, 37.5, 8, 10 Ω , respectively. This shows that Densifier 500 has outstanding potential for the mitigation of corrosion.

Compared to SHS7740, the R_{ct} for Ni-P and Ni-P-TiO₂ is 2750 and 4.5x10⁵ Ω , respectively. This is 10³ to 10⁵ orders difference with SHS7740. Therefore, for the application in sulfuric acid environments, electroless nickel plating shows outstanding performance.

3. Conclusions

As the flow-accelerated corrosion inhibitors in secondary piping system of nuclear power plants, various kinds of nano-structured coatings were prepared and tested in room-temperature electrochemical cells. SHS7740 with two types of Densifiers, electroless nickel plating with TiO₂ are prepared. Electropolarization curves shows the outstanding corrosion mitigation performance of SHS7740 but EIS results shows the promising potential of Ni-P and Ni-P-TiO₂ electroless nickel plating.

For future work, high-temperature electrochemical analysis system will be constructed and in secondary water chemistry will be simulated.

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