Corrosion Characteristics of Nano-structured Coatings for the Application in Secondary Piping System of Nuclear Power Plants

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1. Introduction

Carbon steel is widely used in industry as a pipe. In nuclear power plants, especially, it is used in secondary water chemistry environment [1]. But secondary water chemistry environment is little different from general environment. It has fast flow, high pH, dissolved oxygen control agent like a hydrazine, high pressure and high pressure etc, and these lead the corrosion of carbon steel much severe. So extending using time of carbon steel is important issues in industry.

Coating surface using less corrosive metal is one of methods that reduce electrochemical corrosion. And metal oxide like a TiO_2 is studied because it is stable, insoluble when coating is exposed severe environment [2]. Several coating technics are used for better corrosion resistance. Pysical vapor deposition(PVD), chemical vapor deposition(CVD), thermal spray , electroplating, electroless etc. But thermal spray coating makes thermal stress to substrates because its temperature are more than 3000K. And powder's deformation can occur [3]. And CVD makes decarburization near interface between surface and coating layer [4]. In addition, CVD and PVD needs vacuum chamber. Electroplating is chemical reaction at surface, but it needs electric power. On the other hands, electroless plating dosen't needs electric power and it's temperature is low than thermal spray. Also the pipe dipping into the chemically solution can proceed coating easily.

So, in this experiment, we carried out experiment about Ni-P electroless plating added TiO_2 nano particles for observing corrosion properties compared carbon steel substrates in room temperature as previous research.

2. Experimental

2.1 Preparation

Carbon steel(20mm × 20mm × 5mm, POSCO) was used as substrate and it's chemical composition is in Table 1.The sample were mechanically polished with #320, #400 and #800 grit SiC papers to remove corrosion products and remaining oxides. After mechanical polishing, the samples were cleaned using a deionized water, acetone, NaOH and H_2SO_4

For making electroless Ni bath, chemicals in Table 2. was used. The reason Ni plating bath maintains pH 9 is that zeta potential of TiO_2 nano particles must be less than zero for dispersion [5]. And anionic surfactant, sodium dodecyl sulfate was used for better dispersion.

For seeing surface morphologies, we used scanning electron microscope (SEM). And Energy-dispersive X-ray spectroscopy (EDS) was used to know chemical composition of surface. In electrochemical Experiments, Saturated calomel electrode (SCE) as reference electrode, Pt as counter electrode, As-polished, Ni-P and Ni-P-TiO_2 samples as working electrode and 3.5 wt % NaCl as elecrolyte is used for potentiodynamic electropolarization. Potential range is ±0.3 V versus OCP and scan rate is 2 mV/sec and fitting software is Corrware

Table. 1. Chemical composition of SA 516 Gr.60

Element	C	Si	Mn	P	S	Cu	Ni	Cr	Fe
Wt%	0.13	0.201	0.714	0.0141	0.0041	0.006	0.01	0.006	Balanced

Table. 2. Chemical composition of electroless nickel plating bath

Chemicals	Quantity (g/L)		Role
	Bath A	Bath B	
$NiSO_4 \cdot 6H_2O$ (nickel sulfate)	25	25	Nickel source
$NaH_2PO_2 \cdot H_2O$ (sodium hypophosphite)	20	20	Reducing agent
$Na_3C_6H_5O_7 \cdot 2H_2O$ (tri-sodium citrate)	10	10	Complexing agent
H_2NCH_2COOH (Glycine)	25	25	Brightening agent
$NaC_{12}H_{25}SO_4$ (sodium dodecyl sulfate)	-	0.1	Anionic surfactant
$(NH_4)_2SO_4$ (ammonium sulfate)	27	27	pH buffer
Anatase TiO_2 (< 21 nm)	-	2	nano-particles
pH	9	9	

2.2 Coating procedures

First, Ni plating bath is manufacturing by table 2. Second, TiO2 nano particles is added in bath and mechanically agitated with magnetic stirrer in 200 RPM for 2 hr. Third Ni + TiO2 bath is agitated by using ultrasonic for 1 hr. Forth, substrate is coated in bath for 2 hr in 80°C. Finally, coated samples are heat-treated in furnace in Ar atmosphere for 1 hr in 400°C

3. Results and Discussion

Compare surface morphologies (Fig. 1), surface of Ni-P coated samples have bigger grain than Ni-P heat-treated sample. That indicated that heat treatment effects on coating quality. And coating added TiO_2 nano prticles makes SEM images blurry and many agglomerated particles in surface. That means TiO_2 nano particles act like nucleation spot and Ni-P is agglomerated in this spot. But there is no chemical composition difference between agglomerated spot and flat surface in EDS profiling
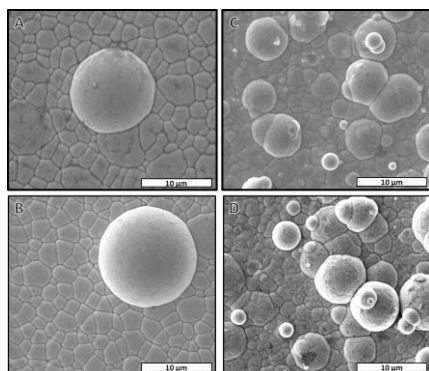

Fig. 1. Images of surface of (A) as-plated Ni-P, (B) heat-treated Ni-P, (C) as-plated Ni-P-TiO2 and (D) heat-treated Ni-P-TiO2 samples

In cross-section morphologies (Fig 2.), Ni-P coating samples have 12 μm coating depth. But Ni-P-nanoTiO$_2$ have 3 to 4 μm coating depth. The reason coating depth difference is probably addition of TiO_2 nano particles. Ni is coated in sample's surface by electrochemical reaction, but TiO_2 is stable in Ni bath. So that makes coating difficult in experiment. After heat-treatment, sample's surface is very rough. That means heat-treatment infects coating and it effects on corrosion resistance.
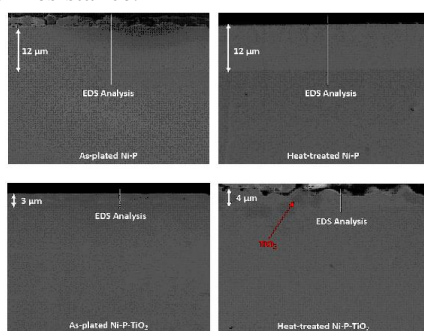

Fig. 2. SEM cross-section morphologies before and after heat-treatment

Room-temperature electrochemical experiments results are in Fig.3 and Table 3. As-polished samples have 1570 Ω /cm^2 corrosion resistance and 1.66×10^{-5} corrosion current density. But Ni-P coating have 3 times bigger corrosion resistance and Ni-P-TiO$_2$ have 5 times bigger corrosion resistance. And corrosion current density is smaller than as-polished samples.

Especially Ni-P heat-treated samples and Ni-P-TiO$_2$ heat-treated samples show better corrosion resistance compared to other samples. So heat-treatment makes corrosion resistance better and this effect is maximized when TiO_2 nano particles are added.
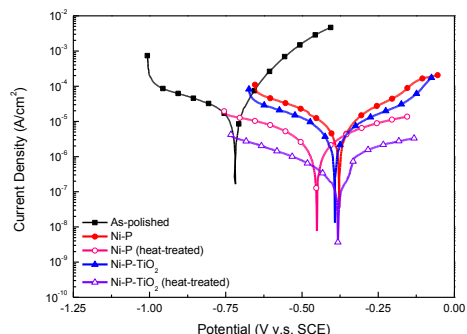

Fig. 3. Potentiodynamic electropolarization curves of the samples in 3.5 wt% NaCl electrolyte

Table. 3. Polarization resistance, corrosion current and potential of the samples

	R_p (Ω/cm^2)	I_0 (A/cm^2)	E_0 (V)
As-polished	1570	1.66×10^{-5}	-0.72
Ni-P	5443	4.79×10^{-6}	-0.378
Ni-P (heat-treated)	20883	1.25×10^{-6}	-0.451
Ni-P-TiO$_2$	8058	3.24×10^{-6}	-0.392
Ni-P-TiO$_2$ (heat-treated)	106000	2.47×10^{-7}	-0.381

4. Conclusions

To reduce FAC, we have experiment about corrosion resistance of electroless Ni-P coated carbon steel in room temperature. And it has possibility of reducing corrosion and addition of TiO_2 nano particles in Ni-P coating layer makes having better corrosion resistance. And results give us a possibility that electroless Ni-P coating added TiO_2 nano particle can have better corrosion resistance compared carbon steel. So it needs study about high temperature corrosion experiment of electroless Ni-P coating added TiO_2 nano particle.

Especially, heat-treatment effects on surface roughness and corrosion resistance significantly. So effects of heat-treatment will have to be studied.

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