Corrosion Performance of Coating for Venturi Fouling Mitigation at Nuclear Power Plant

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1. Introduction

In nuclear power plants, the thermal power of reactor is calculated by the thermal balance equation based on the main feedwater flow rate supplied to the steam generator. The main feedwater flow rate is measured through a venturi flowmeter installed in the main feedwater pipe of the secondary system. However, the venturi flowmeter has a fouling issue. Fouling is a phenomenon in which microparticle suspension such as iron oxide (Fe_3O_4, magnetite) are deposited on pipe walls and near venture holes, thereby changing surface roughness, and causes an error in the measurements of the venturi flowmeter.

Due to the oxide deposit caused by fouling in Korean nuclear power plants, the pressure loss value of the flow rate has increased by 0.3 % every year, which has led to the problem of reducing the power generation of nuclear reactors [1,2]. In addition, economic losses are incurred through the cleaning or replacement of the venturi flowmeter during the regular planned preventive maintenance [1].

Up to this time, the studies on venturi fouling conducted in Korea have such a limitation that only structural modification of the venture design or changing operation methods have been performed [2,3]. It has been reported that General Electric company (GE) in the United States solved the fouling phenomenon in the jet pump pipe of the boiling water reactor (BWR) by applying a TiO_2 coating technology [4].

Therefore, we apply various metal surface coating technologies such as physical vapor deposition (PVD) and electroless plating, so as to reduce the deposition of iron oxide inside the venturi system, to increase the operating time of the venturi, and to minimize the error in main feedwater flow rate measurement. Corrosion performance testing is mainly reported in this work.

2. Experimental Procedures

2.1 Specimen Preparation

The specimens used in this study were commercial 304L stainless-steel with 10 mm x 25 mm x 2 mm. The chemical composition of them is shown in Table I. All surfaces of each specimen were mechanically ground with silicon-carbide papers up to 800 Grit, and then ultrasonically cleaned in ethanol and deionized water for 5 min and dried. In a broad sense, two techniques of coating were used. First, CrN, Ti, and TiN were deposited by PVD coating technology. Second, the Ni and Pd were deposited onto specimens using an electroless plating method.

Table I: Chemical composition of Test Material (wt.%)

C	Si	Mn	P	S	Cr	Mo	Fe
0.03	0.32	0.46	0.011	0.004	16.00	3.00	Bal.

2.2 Static Corrosion Test

The experiments were conducted in a static autoclave operating at 235℃ in secondary water chemistry condition, at a saturation pressure of 27 bar. Fig. 1 shows the static autoclave system. The pH=9.3 of simulated secondary water condition was adjusted with ETA. And then, 60 ppb hydrazine was added to the solution. Also, carbon steel pieces were put in to simulate Fe injection. The pieces were divided into 4 parts of carbon steel with a diameter of 25 mm and a thickness of 2 mm. The solution was deaerated using Ar gas for the initial 2 hours, maintained at 130 ℃ for 2 days to sufficiently dissolve Fe in the test water. Then, the temperature was raised to 235℃, and experiment was conducted for 300 hours.

Fig. 1. Static autoclave corrosion test apparatus.

2.3 Flow Accelerated Corrosion (FAC) Test

The test facility for simulating the secondary water chemistry condition is shown in Fig. 2. The test facility consists of water chemistry control and monitoring system and Magnet drive rotating system for simulating the high flow rate as FAC test. The test solution was the same as static corrosion test solution. However, the pressure was set to 82 bar, which is the same as the secondary water condition. The accelerated flow rate was

set at about 6 m/s. The FAC experiment was conducted for 700 hours.

Fig. 2. Flow accelerated corrosion test facility.

2.4 Microstructure Characterization & Mass Change

The surface and cross-section of specimens were observed by field emission scanning electron microscopy (FE-SEM, Mira3, Tescan) at 15 kV, while the chemical composition was evaluated using an energy dispersive X-ray spectroscopy (EDS, X-max, Oxford).

The crystal structures were analyzed by X-ray diffraction (XRD, Ultima IV, Rigaku) using Cu-Kα radiation at 40 kV/20 mA. The diffraction patterns were scanned at 20–80° with a 0.02°/s.

Mass change is the method to evaluate the corrosion rate by measuring the mass change of samples before and after the corrosion test. The specimen is immersed in the test solution for a period, after which retrieved and the change in mass is measured. The following is the formula to calculate corrosion rate:

$$R = \frac{W}{At\rho} \qquad (1)$$

where R is the corrosion rate, W is the change of mass, A is the original surface area exposed to the corrosive media, t is the exposure time, and ρ is the standard density of the sample.

3. Results and Discussion

3.1 Corrosion Rate from Mass Change

After the static and FAC test, each coated specimen was ultrasonically washed for 20 minutes in the order of acetone, ethanol, and distilled water. Thereafter, after drying the specimen fully, the mass change of specimens was measured. The corrosion rate was calculated through the measured mass change. Fig. 3 shows the corrosion rate calculated from the mass change of the specimen after the static test. The specimen coated with the PVD method had a relatively low corrosion rate. On the other hand, the specimen deposited by Ni indicates the highest corrosion rate.
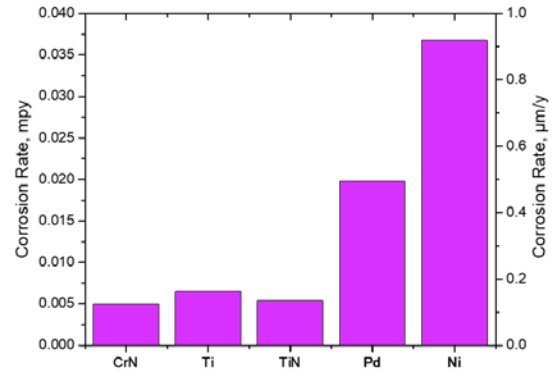

Fig. 3. Corrosion rate calculated from static corrosion test.

Fig. 4 shows the corrosion rate for the specimen after the FAC test. These results also show that the corrosion rate of the specimen deposited by Ni was the highest.

The reason why the specimen deposited by Ti-based coating has a relatively low corrosion rate is Ti is an active metal and has very high reactivity and is oxidized rapidly. Especially, it is known that the TiO_2 oxide film through the oxidation reaction has excellent corrosion resistance due to its passivation property. On the CrN coated specimen, an oxide film of Cr_2O_3 is formed, which has an electrically stable passivation property upon oxidation. Therefore, it shows a low corrosion rate. Pd is a very noble metal with good corrosion resistance. However, the specimen used in this experiment had partially cracked on the surface even before the experiment. [5] Therefore, it was considered that the palladium oxide film could not be formed due to the existing crack during the corrosion test, and the mass change was largely due to the falling off of the Pd layer.

Although Ni is also known to have excellent corrosion resistance at high temperatures, the corrosion rate was high. However, since this corrosion rate result was calculated as a result of short-term experiments of 300 hours and 700 hours, respectively, the initial corrosion rate appeared somewhat higher. If the experiment is carried out over a period of several months or longer, the corrosion rate will be significantly lower for all types of coated specimens.
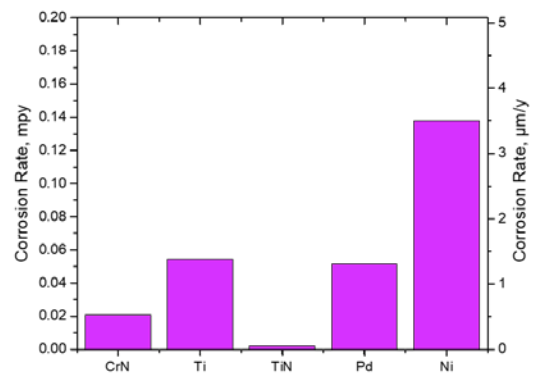

Fig. 4. Corrosion rate calculated from Flow accelerated corrosion test.
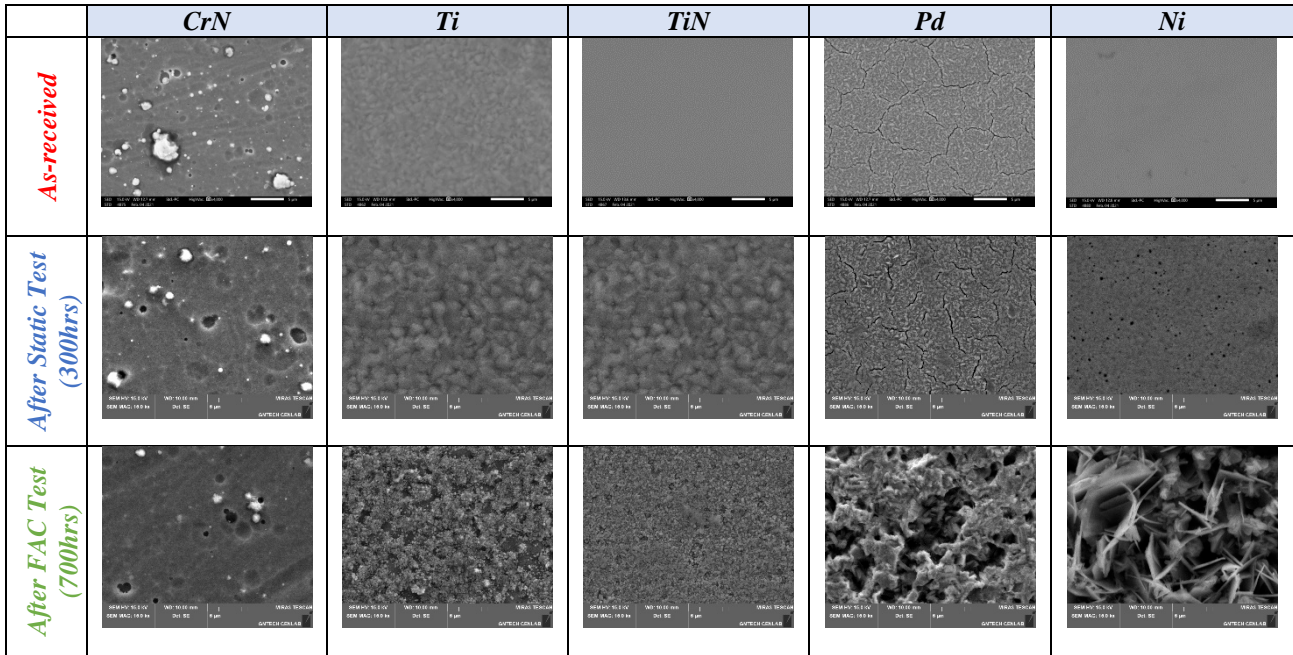
Fig. 5. SEM images for the surface of Samples (As-received, After Static Test, and After FAC Test).

3.2 Surface Morphology

Fig. 5 shows the surface before and after corrosion tests of coated specimens of five materials. In general, as CrN is known to have good stability in the secondary environment of nuclear power plants, there was no significant difference in the surface after static or FAC test. This is because Cr quickly formed a Cr_2O_3 oxide film regardless of the duration of the corrosion test.

The surface coated with Ti or TiN was smooth before the experiment. However, after 300 hours of static experiment, TiO_2 nanoparticles were generated on the surface. The surface after the FAC experiment revealed that a maximum size of several micrometers of TiO_2 particles and higher number density of particles compared with the case of the static test. This suggests that as the corrosion period increases, the TiO_2 particles become larger.

When Pd corrodes, PdO forms and becomes a very dense and stable state. However, in the FAC test, the existing crack fell off due to the flow and changed into a porous structure. If the specimen was completely coated with Pd without cracking on the surface, it is considered that the surface with a dense structure was observed. In the case of Ni, it shows that NiO was formed on the surface after the FAC experiment. On the other hand, after the static test, only Ni oxide particles were found on the surface, but there was no significant difference in surface shape.

3.3 XRD Analysis

Fig. 6 shows the results of XRD analysis on the specimen after the static test. CrN coated specimens showed that Cr_2O_3 was formed. However, other types of oxides were not identified on any other specimens. This suggests that the Cr oxide film forms more easily and quickly. Also, it is considered that TiO_2 or NiO particles identified during SEM-EDS analysis on the surface were too small to be detected by XRD analysis.
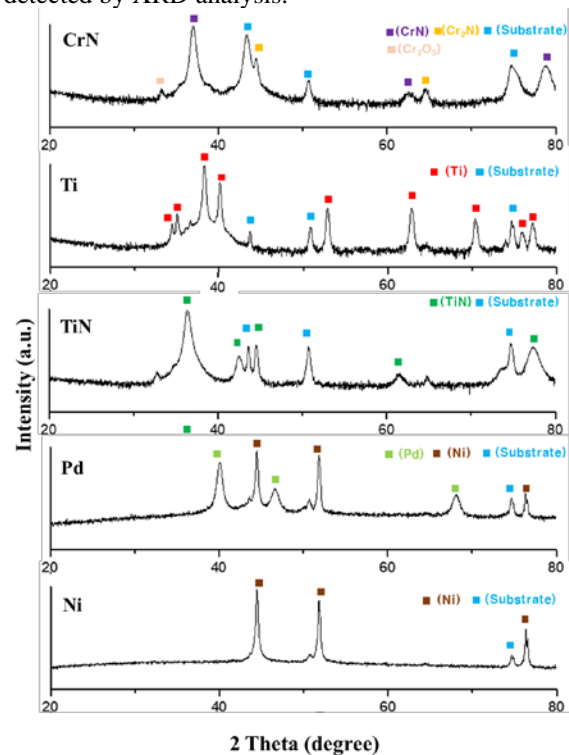

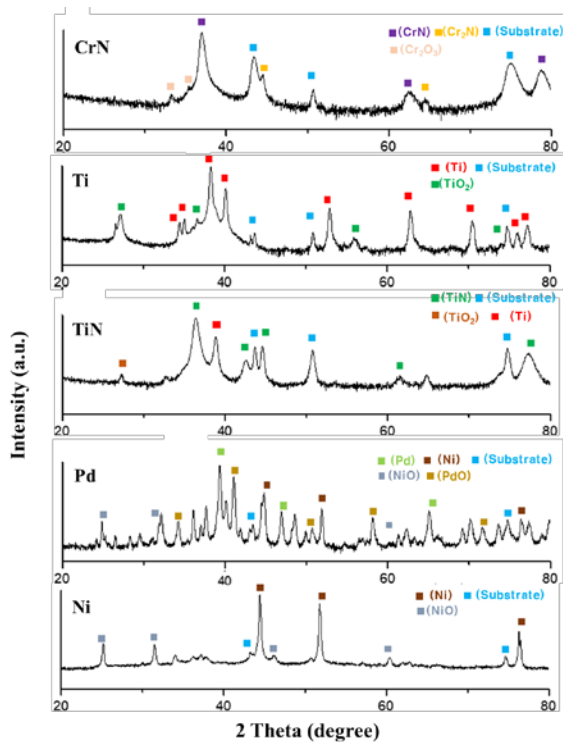Fig. 6. XRD results of specimens conducted by static test at 235℃ during 300 hrs.

Fig. 7. XRD results of specimens conducted by FAC test at 235℃ during 700 hrs.

Fig. 7 shows the results of XRD analysis on the specimen after the FAC test. After the FAC test, oxidation reactions occurred actively in all specimens. TiO_2 oxide film was detected in the specimens coated with Ti or TiN. That is, it can be seen that 700 hours is a sufficient period for the formation of the oxide layer of the coated specimens. Also, the Pd coating has a double-layer structure with Ni coating inside. XRD results show that PdO and NiO were formed. [5] This is because Pd on the upper side falls off due to the influence of accelerated flow, and Ni is oxidized to NiO.

4. Conclusions & Future Work

The purpose of this study is to develop a method for mitigating the fouling phenomenon occurring at the venturi flowmeter in the secondary side of nuclear power plants. Various coatings deposited on 304L stainless-steel and their corrosion resistance properties were evaluated in the simulated PWR secondary water chemistry condition using static and FAC tests. After the testing, all of the specimens were characterized by SEM-EDS and XRD.

As a result, Ti or TiN coating formed a dense coating layer without defects on the surface by the PVD method. TiO_2 oxide film was formed after 700 hours of the FAC test, but only microparticles were formed after 300 hours of the static test.

In the CrN coating by PVD, surface defects such as pinholes and fine droplets were found on the as-received surface, which can be, however, removed by the process modification. Also, Cr is easily oxidized even in a static

autoclave experiment of only 300 hours, and a passive film of Cr_2O_3 was formed. Ni also showed no significant change in the static test. However, the corrosion rate calculated from the mass change showed the highest. These results need to be verified through long-term corrosion tests in the future. Also, the existing crack in Pd had a falling effect on the corrosion test result.

Overall, the PVD coating method has excellent quality of the coated material, but when the structure of the coating material has a geometric structure, it is difficult to apply the coating material or obtain a uniform coating surface. Therefore, the PVD coating method is intended to be applied when the structure of the venturi flowmeter is changed and applied in a new design nuclear power plant. It is planned to apply electroless plating that can ensure uniform coating quality while maintaining the existing geometric design in the operating nuclear power plant.

Therefore, in the future, we plan to perform long-term corrosion performance tests on coated specimens in the same water chemical environments as the nuclear power plant secondary system. This includes performing a Pd that is free of cracks coating using the electroless plating method.

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