# The influence of Zn nanoparticle treatment on the stress corrosion cracking resistance of the 304 stainless steel

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## 1. Introduction

Many studies have reported that $Zn^{2+}$ injection effectively mitigates the primary water stress corrosion cracking (PWSCC) of 304 stainless steel since composition and structure of oxide films can be modified by Zn [1-2]. However, other corrosive ions ($OH^-$ and $CO_3^{2-}$) can be generated when Zn injection was conducted by using Zn precursors such as dimethyl zinc, diethyl zinc, zinc hydroxide, and zinc carbonate. In this study, Zn nanoparticles as protective agent of PWSCC were synthesized by the method of plasma discharge in aqueous solution. The superior properties of this method are the high rate of reaction and no requirements of thermal and pressure owing to the high active species generated during discharge [3]. Also, this method does not employ any chemical agent when nanoparticle was synthesized in solution. The synthesized Zn nanoparticles in solution were applied for the treatment of 304 stainless steel at simulated pressurized water reactor (PWR) environment (300 ℃, 150 bar).

## 2. Method and Results

### *2.1 Zn nanoparticles synthesis*

Zn nanoparticles were synthesized by the method of plasma discharge in aqueous solution. The solution plasma was created at the gap between electrodes by controlled plasma conditions using bipolar pulsed power supply (MPS-06K06C, Kurita-Nagoya, Japan). As shown in Table I, the typical parameters including voltage, frequency, pulse duty, discharge time, electrode type and electrode gap were set to be 2400 V, 20 kHz, 10−85%, 600 sec, pure Zn electrode (2Φ) and 1.0 mm, respectively.

Table I: Experimental conditions of plasma discharge in aqueous solution

| | |
|---|---|
| Power type | Bipolar pulsed |
| Voltage | 2400 V |
| Frequency | 20 kHz |
| Pulse duty | 10-85 % |
| Discharge time | 600 sec |
| Electrode type | Pure Zn electrode (2Φ) |
| Electrode gap | 1.0 mm |

### *2.2 Materials*

The 304 stainless steel which is widely used in pipelines of the nuclear power plant's reactor coolant system was used to examine the SCC prevention behavior by Zn nanoparticle treatment.

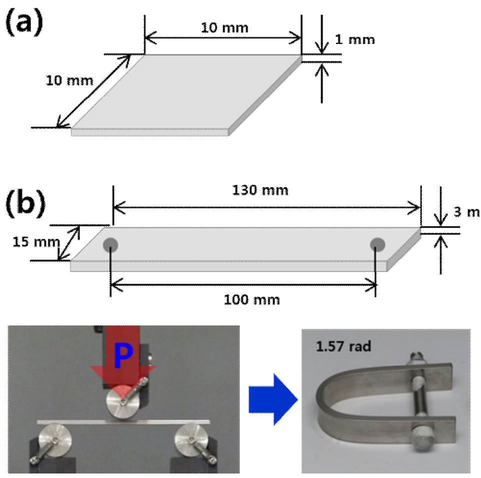


Fig. 1. Schematic of specimens for corrosion potential test & XRD, XPS analysis (a) and U-bend sample for SCC prevention test in simulated PWR condition (b).

As shown in Fig.1 (a), the specimen was prepared with the plate type stainless steel 304 (10 mm X 10 mm X 1 mm) for corrosion potential test and the structures of oxide films analysis. U-bend type stainless steel 304 (130 mm X 15 mm X 3 mm) was used to investigate the SCC prevention behavior in simulated PWR condition (300 ℃, 150 bar) as Fig.1 (b). The specimen of U-bend type stainless steel 304 was fabricated by the standard of ASTM G30-97.

### *2.3 Zn nanoparticle treatment on the 304 stainless steel*

The pipe type stainless steel 304 was used to simulate the PWR system. The dimensions of piping system were 89.1 mm in diameter, 7.6 mm in thickness and 150 mm in length.

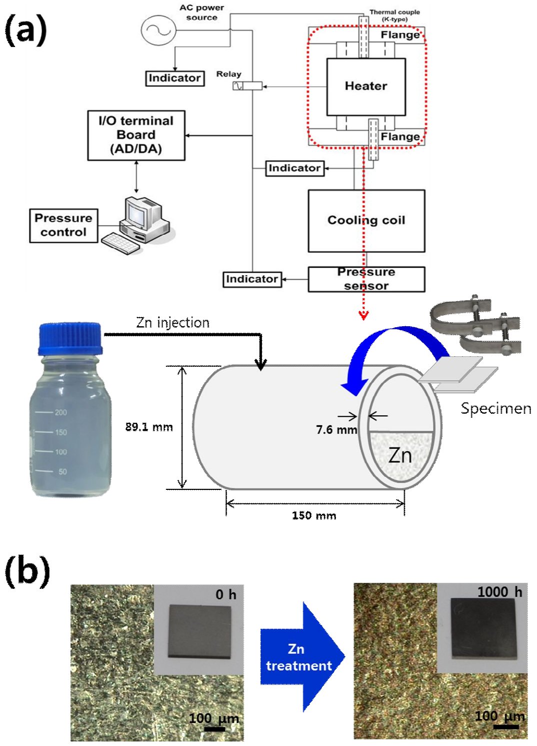
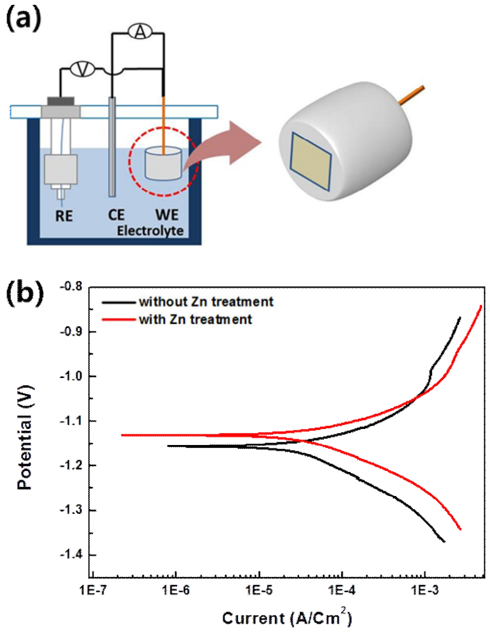


Fig. 2. Diagram of equipment for Zn nanoparticles treatment under PWR simulating environment (a) and optical microscopic images owing to Zn nanoparticles treatment on the plate type stainless steel 304 specimens (b).

As shown in Fig. 2 (a), this equipment was composed to treat Zn nanoparticles on the plate and U-bend type specimens under simulated PWR condition (300 ℃, 150 bar). After these specimens and Zn nanoparticles of 1.0 M were located in piping system, it was heated using a ceramic heating coil. The simulated PWR condition (300 ℃, 150 bar) was controlled by vapor temperature. Through Zn nanoparticles treatment, the surface chemical composition of plate type stainless steel 304 specimen was changed as Fig. 2 (b).

### *2.4 Corrosion Potential Test (Tafel method)*

The Zn-treated and non-treated plate type 304 stainless steel specimen were subjected to very harsh corrosion test, in which the conditions were $Na_2S$ of 1.0 M and NaOH of 1.0 M. The experiments were performed with the plate type 304 stainless steel (10 mm x 10 mm x 1 mm) to measure the corrosion behavior of it using a Potentiostat/Galvanostat (EG&G 263A, PAR) as shown in Fig. 3 (a). The counter electrode was a Pt wire and the reference electrode a saturated calomel electrode (SCE). All the potentials are referred to SCE. The potential scan rate of the working electrode was 1 mV/s, which appeared to be sufficiently slow to consider the polarization curves to have been obtained under a quasi-steady state condition [4].



| | Without Zn treatment | With Zn treatment |
|---|---|---|
| Corrosion potential (V) | -1.187 | -1.136 |
| Corrosion current density (µA) | 252.6 | 51.65 |
| Corrosion rate (mpy) | 3.15 | 0.65 |

Fig. 3. Schematic of corrosion potential test; RE (Reference Electrode), CE (Counter Electrode), WE (Working Electrode) (a) and the results of corrosion potential test using by Tafel method (b).

The results from corrosion potential test showed that the corrosion rate of the plate type 304 stainless steel was 5 times retarded through Zn nanoparticles treatment under simulated PWR condition (300 ℃, 150 bar). Consequently, with increasing Zn nanoparticles treatment, the $E_{corr}$ increased and the current density decreased as Fig. 3 (b).

### *2.5 Investigation of oxide film*

To clarify the influence of Zn nanoparticles treatment on the characteristics of the oxide films formed on the 304 stainless steel, the structures and chemical compositions of oxide films were investigated using X-ray diffractometry (XRD), and X-ray photoelectron spectroscopy (XPS) techniques. To investigate the oxide film, the plate type specimens were prepared with the variable of that the Zn nanoparticles treatment duration was controlled in the range from 120 to 1,000 hours. As shown in Fig. 4 (a), diffraction pattern exhibited that stable oxide films with a spinel structure of $ZnCr_2O_4$ would form with increasing Zn treatment duration. According to the diffraction pattern, formation of Zn spinel structure appeared after the Zn nanoparticles treatment during 240 hours for the first time. At that time, the result from XPS Depth profile analysis showed that oxide films with a spinel structure of $ZnCr_2O_4$ were formed about 65 nm thickness as Fig. 4 (b).

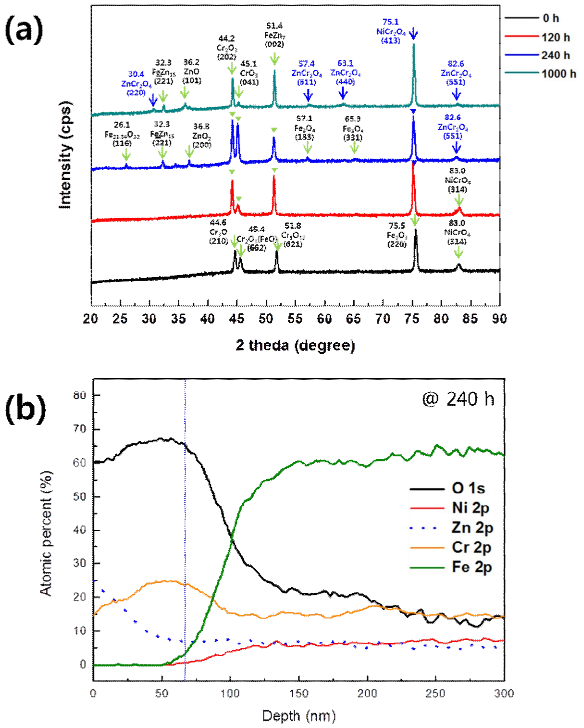
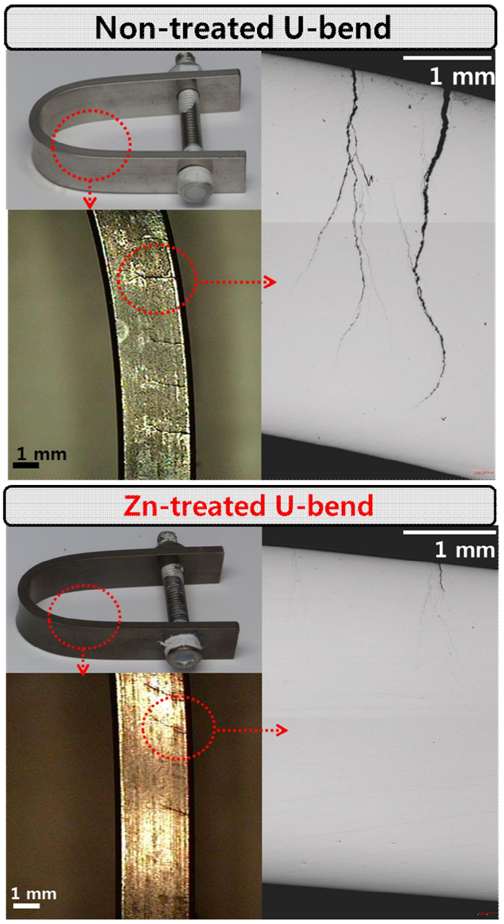


Fig. 4. X-ray diffraction pattern of the oxide film on the plate type 304 stainless steel owing to Zn nanoparticles treatment time (a), XPS Depth profile of the oxide film after the Zn nanoparticles treatment during 240 hours (b).

It is postulated that the exchange reaction between Zn and Fe/Ni cations occurred extensively so that the dense and compact Zn spinel structure responsible for the corrosion inhibition formed [5].

### *2.6 U-bend test*

To confirm the SCC prevention by Zn nanoparticles treatment, U-bend type stainless steel 304 specimens was investigated to very harsh corrosion environment, in which the conditions were $Na_2S$ of 1.0 M and NaOH of 1.0 M under simulated PWR condition (300 ℃, 150 bar). With Zn nanoparticles treatment, total number and length of crack was reduced on U-bend surface as Fig. 5. In other words, Zn nanoparticles treatment exhibits the SCC prevention under residual stress and harsh corrosive environment.



| | Non-treated U-bend | Zn-treated U-bend (1000 h) |
|---|---|---|
| **Total number of crack** | **96 EA/sample** | **15 EA/sample** |
| **Max crack length (on surface)** | **2.768 mm** | **1.724 mm** |
| **Average of crack length (on surface)** | **1.976 mm** | **0.945 mm** |

Fig. 5. Optical microscopic images of U-bend specimens surface owing to Zn nanoparticles treatment.

## 3. Conclusions

The Zn nanoparticles were successfully synthesized using the method of plasma discharge in aqueous solution. After the Zn nanoparticles treatment, the spinel structure was formed at the surface of the 304 stainless steel specimens, which contained the $ZnCr_2O_4$. SCC generation time was delayed after the Zn nanoparticles treatment under residual stress and corrosive environment, and this method could be applicable for the prevention of SCC in the PWR in nuclear power plants.

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