Characteristics of nano-sized TiO_2 for an inhibitor of SCC

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1. Introduction

In nuclear power plants, steam generator (SG) tubes have certain characteristic features in their design to endure a severe problem, a stress corrosion cracking (SCC). Most SCCs have been occurred near the top of a sludge pile on a tubesheet and within a tube support plate crevice in which it is thought to be concentrated by ion impurities such as sodium which might cause a caustic and corrosive environment [1]. Some inhibitors have been studied to reduce these SCC problems for SG tube materials [2-7]. Laboratory tests using C-ring and constant extension rate specimens have shown that some chemical compounds may inhibit a SCC of the SG tube materials. Several titanium compounds have been tested for their application to certain types of PWR nuclear power plant's SGs, such as Prairie Island 1 and 2, Point Beach 2, Callaway 1 etc [8]. While, it has been reported that these are some beneficial effects, there is not enough evidence as yet that would convinced us of its positive effects as an inhibitor, and also, it has not been fully proven that Ti-compound can penetrate through a closed crevice or crack tip in a SG tube. The technology for the smallest scale in nature, nano-technology, has been advanced and has become an important branch in the current science. Many studies have reported on techniques for the production or fabrication of nano-particles and nano-structures [9]. The sonochemical synthesis process was adapted in our study for the reason of its direct applicability to a liquid phase solution. Ultrasound in the liquid containing reactants causes a sonochemical reaction producing nano-particles [10-12]. In this research we investigated an application of a sonochemistry technique to the TiO_2 to reduce its particle size in order to improve its penetration property in a crevice of a SG and its performance on a SCC of the SG tube materials.

2. Methods and Results

The size of the TiO_2 (P25) particle was reduced by a sonochemical method in distilled water. 'P25' means a product number of TiO_2 manufactured in Evonik-degussa industries. In the sonochemical process, the ultrasonic power was 750 Watts with a frequency of 20 kHz using a VC750 ultrasonic process machine (Sonics Inc.). A solution of TiO_2 (P25) was cooled to room temperature during the ultrasonic treatments. The process was conducted at the condition of a varying time and an amount of 10% ethyl alcohol was added to the water. After the ultrasonic process, the TiO_2 (P25) particle was analyzed by the 90 Plus particle size analyzer produced by the Brookhaven Instruments Co. From this analysis, the effective diameter and zeta potential of the TiO_2 (P25) particle were obtained vs. the ultrasonic process time in hours. The particle shape was investigated using the TEM photograph. Using the RUB specimens, the SCC properties of the SG tube materials were tested with each sonochemical processed TiO_2 (P25). SCC tests were carried out to investigate the performance of several chemicals including TiO_2 with SG tube materials such as Alloy 600 MA, TT, HTMA, Alloy 690 and Alloy 800. The used specimen was a modified reverse U-bend (RUB) in the SCC tests that were performed in a 10% NaOH solution at a temperature of 315℃. The RUB specimen was insulated by using zirconia parts and it was preloaded by a 20% tensile strain gauge length before being bent. During the SCC tests, the RUB specimens were checked by an optical stereomicroscope.

From the XRD analysis, TiO_2 (P25) was composed of a crystal structure of an anatase and rutile form with a ratio of 82:18. One group of the anatase structures was formed in the range of a particle size of about 0.04 ~ 0.08 ㎛ in diameter and another peak of a rutile structure was formed in the range of 0.8 ~ 2.0 ㎛ in a diameter. As shown in Fig. 1, the effective diameter of the TiO_2 (P25) powder was decreased to a value of about 130 nm with an ultrasonic process time over 10 hrs from about 400 ~ 800 nm in diameter. The zeta potential was changed in the range of ~ 55 to 60 mV. The variation of the zeta potential could affect the colloidal properties of the particles in a liquid phase.

The results of the SCC tests with nano-sized TiO_2 (P25) showed an improvement of the resistance to a cracking (Fig. 2). The application of nano-sized TiO_2 (P25) improved the SCC resistance by more than 20% when compared to the addition of TiO_2 (P25) which was not nano-sized in the test for the Alloy 600 materials. The thickness of the oxide layer was reduced and also the property of the surface was changed by the addition of nano-sized TiO_2 (P25). The surface of the specimen after the SCC test was brighter with the addition of more sonochemically processed TiO_2. It is expected that the improvement of the penetration through the crevice, and the increase of the surface area, might cause the increase of the chemical reaction between the oxide layer and the water in the crevice.

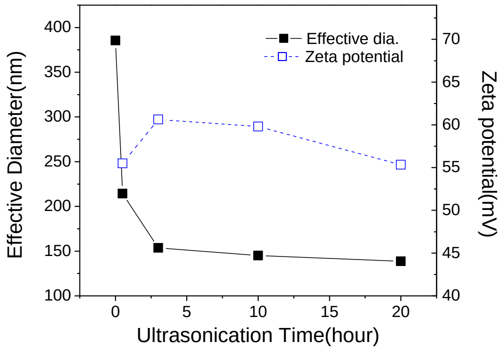

Fig. 1 Effective diameter and zeta potential of the TiO_2 (P25) with the ultrasonic process time in hours.

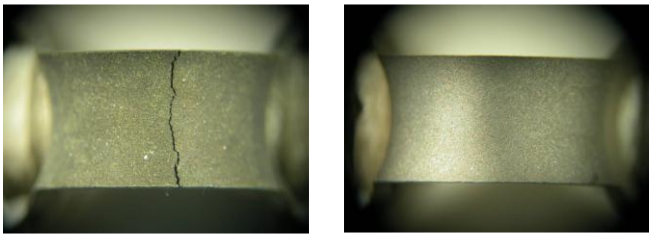

Fig. 2 Top view of the Alloy 600 MA specimen surface after 40 days SCC tests in a soulution of 10% NaOH at 315℃ with (a) TiO_2 0.1 g/L(Ultrasonic-treated Time;UT 1 hrs) (b) TiO_2 1 g/L (UT* 10 hrs).

3. Conclusions

The tests with the additions of TiO_2 revealed a decrease in the SCC rate of the SG tubing materials. From the analysis of the fracture surface and the electrochemical property of the oxide layer, the addition of TiO_2 could form a more stable oxide film and it might improve the resistance of the tube materials to a SCC. The effective diameter of the TiO_2 powder was decreased to a value of about 130 nm with an ultrasonic process time over 10 hrs, and the zeta potential was also changed. The results of the SCC tests with nano-sized TiO_2 showed an improvement in the resistance to a cracking.

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