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Boric Acid Corrosion of RPV Head Materials in PWR

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1. Introduction

Recently, corrosion damage in the reactor pressure vessel (RPV) head, penetration nozzles and their welds in pressured water reactors have been found throughout the world [1]. The RPV head, SA508 with a carbon content of about 2 wt%, for the nuclear power plant is fabricated from forging and/or heavy plates. It is known that SA508 could be very susceptible to a corrosion in boric acid solutions and/or salts [2,3]. In the present work, corrosion behaviors of SA508 in a boric acid solution were studied as a function of the boron concentration, temperature and test duration.

2. Methods and Results

2.1 Experimental Procedures

The alloys used in this study were taken from the archive materials of Ulchin 3 Unit (U3) and Youngkwang 5 Unit (Y5), and it was confirmed that the alloys satisfied ASTM SA508 Grade 3 Class 1 requirements. Before a corrosion test, a microstructural examination of the alloys was conducted by an optical microscopy and scanning electron microscopy (SEM). The test specimens with dimensions of 15 x 15 x 1.5 mm were immersed in a boric acid solution, and the weight loss after a test duration was measured. A corrosion rate expressed as millimeters per year (mm/yr) was calculated from the measured weight loss. After a corrosion test, corroded surfaces and corrosion products were analyzed by SEM, X-ray and transmission electron microscopy (TEM).

2.2 Microstructures

Fig. 1 shows the typical microstructure of U3 alloy taken from SEM. It was found from the chemical and X-ray analyses that the U3 and Y5 alloys had almost the same chemical composition, crystal structure, density, and precipitate type/shape/distribution. In the figure, coarse and irregular precipitates were distributed along the grain boundaries, and needle-like ones were found inside the grains. All the precipitates found in SA508 were identified as iron carbides by a TEM analysis. The only difference in the two alloys was an average grain size. The average grain size of U3 alloy was much greater than that of Y5 alloy.

From the examination of the corroded surfaces after the corrosion test, it was revealed that only general corrosion occurred without any selective and/or localized corrosion such as a pitting and cracking.

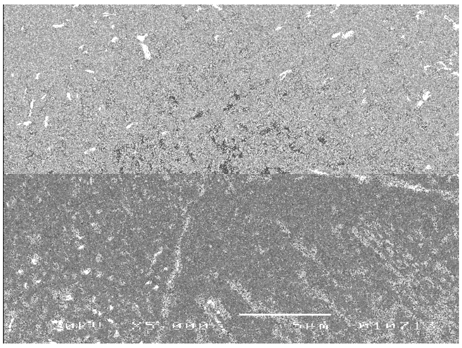

Figure 1. SEM micrograph showing the precipitate morphology of U3 alloy.

2.3 Corrosion Behaviors

Throughout the test, it was found that the results were highly reproducible and reliable, and the corrosion rate of Y3 alloy was always greater than that of U3 alloy. It can be concluded that the different corrosion rates of two alloys could originated from the difference in microstructure such as the average grain size and dislocation density/distribution.

As the boron concentration increased, the corrosion rate also increased monotonously, as shown in Figure 2. The test was conducted under an aerated condition at 90 ℃ for 3 days.

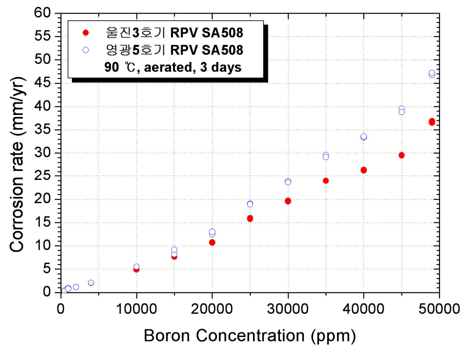

Figure 2. Corrosion rates of U3 and Y5 alloys as a function of boron concentration tested at 90 ℃ for 3 days.

The effect of the test duration could be divided into 2 categories. The corrosion rate slowly decreased during the test period, or it rapidly decreased at the early stage and then converged to a certain value after a long time.

Figure 3 gives the corrosion behaviors of the alloys depending on the temperature. The corrosion rate increased gradually, and then decreased abruptly at a certain temperature. This tendency became less remarkable as the concentration of the boric acid became getting high, and finally disappeared when the boric acid was saturated. The reason could be deduced from the fact that, as the temperature was changed, the oxidation reaction on the surface could also be changed due to a different dissolved oxygen content, therefore a different corrosion product formation on the surface.

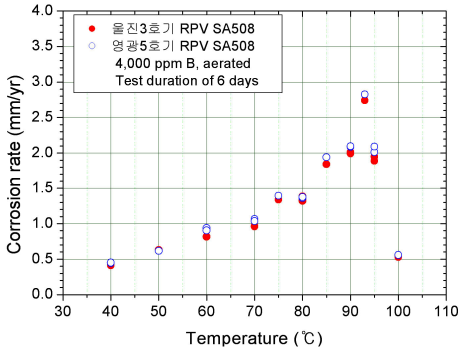

Figure 4. Corrosion rates of U3 and Y5 alloys as a function of temperature under the aerated condition with boron concentration of 4000 ppm for 6 days.

2.4 Corrosion products

Figure 4 shows X-ray peaks of the corrosion products, tested at 95 ℃ with a boron concentration of 4000 ppm for 3 days. From the analysis, the corrosion products were identified as hematite (Fe_2O_3). In the present study, 3 different types of corrosion products were found, that is, hematite (Fe_2O_3), magnetite (Fe_3O_4), and iron oxide hydroxide (FeOOH).

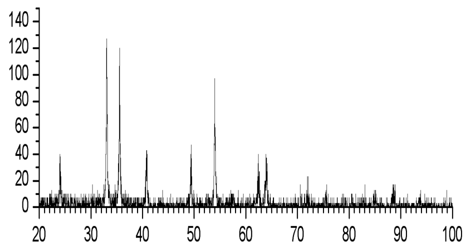

Figure 4. X-ray peaks of the corrosion products, tested at 95 ℃ with a boron concentration of 4000 ppm for 3 days.

3. Conclusion

SA508, as an RPV material, showed typical general corrosion characteristics in boric acid solutions. Y3 alloy had higher corrosion rates than that of U3 alloy because of a different microstructure. The corrosion rate increased monotonously as the boron concentration increased. As the exposure time increased, the corrosion rates slowly or rapidly decreased, according to the oxidation reaction type on the specimen surface. The corrosion rates showed a complicated pattern depending on the temperature, that is, it increased gradually, and then rapidly decreased again at a certain temperature. Finally, the corrosion products were identified as Fe_2O_3, Fe_3O_4, and FeOOH.

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