Corrosive Wear of Alloy 690 Tubes in Alkaline Water

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The interaction between wear and corrosion can significantly increase total material losses in water chemistry environment. The corrosive wear tests of a PWR steam generator tube material (Alloy 690) against the anti vibration bar material (409 SS) were performed at room temperature. The tests were performed in alkaline water chemistry conditions. NaOH solution was selected for test condition to investigate the corrosive wear effect of steam generator tube material in alkaline pH condition without other factors. The flow induced vibration can caused tube damage and the corrosion can be occurred by water chemistry. The test results showed that, in the alkaline solution at pH 13.9, the corrosion current density was increased about ten times than that in the distilled water. And wear rate at pH 13.9 was increased about ten times from that at neutral condition. However, the wear rate was decreased with time. The decrease would be attributed to the change in roughness of specimen or sub-layer of the worn surface with time. From microstructure observation, severe abrasive shape and several wear debris were found. From those results, it could infer that the oxide film on Alloy 690 changed to easily breakable one in the alkaline water, and then abrasion with corrosion became the main wear mechanism.

Keywords: corrosive wear, alloy 690 tube, alkaline water, NaOH solution, oxide film, fretting wear

1. Introduction

The various kinds of degradation phenomena that may occur in the steam generator are affected by thermal hydraulics and a number of corrosion processes. Most utilities operate their units on all volatile treatment (AVT) chemistry, where the pH is controlled by adding an adequate amount of chemicals to the bulk water. During the operation water flow induces the tube vibration in the U-bend region of steam generator tubes known as the flow induced vibration.

From the Ko's study, wear damage of steam generator tubes was considered as one of the most severe degradation in PWR plants. And, since early 70's, many empirical models have been proposed from wear tests of steam generator tube. Recently, the work rate model was proposed by Frick, et al. (1984) and used widely for the fretting wear analysis of steam generator tubes. The work rate model was derived from Archard's wear equation. The model defined the work rate $W^d$ as

$$W^d = \frac{1}{t} \int F\,ds$$

(1)

where $F$ is contact normal force, $s$ is sliding displacement and $t$ is time. Then, the volume wear damage rate can be expressed as

$$V^d = K W^d$$

(2)

where $K$ is the wear coefficient. This coefficient was generally used to evaluate the durability of steam generator tube from wear damage. The flow induced vibration causes wear damage on the steam generator tubes against their support structures, and the wear and corrosion combined action results in mutual reinforcement. The interaction among abrasion, rubbing, impact and corrosion can significantly increase total material losses, especially in aqueous environment. The effect of wear on corrosion was founded to be related to the recovery rate of passive films broken by scratching. And the pure abrasion rate increased with decreasing pH.

For Korean PWR, Kori 1 changed the steam generator tube material from Alloy 600 MA to Alloy 690 TT and the anti vibration bar (AVB) from 405SS to 409SS. In the later PWRs, Alloy 690 has been used as the tube materials. After changing the material from Alloy 600 to Alloy 690, corrosion related degradations of steam generator tube, especially primary water stress corrosion

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2. Experimental procedures

2.1 Experiment rig and test specimen

The test rig was constructed for the fretting wear test between the steam generator tube material and the anti-vibration bar (AVB) material in water solution condition. Steam generator tube specimen was installed at oscillation motion part, and AVB specimen was attached at normal load applied part. All parts of holders which were contacted with specimens were isolated from specimen by plastic coating or plastic part.

Alloy 690 TT was used as wear test material against 409 stainless steel. The dimensions of the tube specimen were 19 mm in diameter and 12 mm in length and the counter-specimens were prepared from the flat strip. From reports,8),9),10) Table 1 shows the density, the chemical compositions and the mechanical properties of alloys.

2.2 Test procedure and analysis

The experiment was performed with a fretting motion between tube and AVB material. From report,11) Loading frequency of 20 Hz was chosen for the test since it was reported that there was apparently no effect of frequency on wear in the 20 - 35 Hz range. The sliding amplitude was 450 μm and the normal load was set to 20 to 150 N. The test time was 10^5 cycles. And wear tests in 10% NaOH solution, at pH 13.9, were performed to investigate the corrosive wear effect as compared with tests in distilled water, pH 7.

The wear rate was estimated by measuring the weight loss of specimen before and after the experiment and converting to volume loss rate using density of Alloy 690. The specimen was cleaned with acetone in the ultrasonic cleaner and dried with compressed air. To reduce the measurement error, specimens were measured 5 times and standard weight was used before weight measuring. And the work rate was calculated from measured normal loads by LVDT and test displacements.

To infer the wear mechanisms and to analysis the wear particle layer composition, worn surface were observed through the scanning electrode microscope (SEM) and EDX analysis was performed. Before observation, specimens were cleaned with acetone in the ultrasonic.

Through the potentiodynamic test at different pH conditions, the corrosion activity rate on the specimen surface was inferred. The scan rate was 1 mV/s from -1.5 V to 1.5 V. And 30 minutes cathodic cleaning was performed before test. Electrochemical tests were carried out several times for reproducibility.

3. Results and discussions

3.1 Fretting wear in alkali water chemistry condition

Table 1 shows the density, the chemical compositions and the mechanical properties of test specimens.
pH condition.

From this difference of wear coefficient, the oxide composition change on the specimen surface of alloy 690 could be inferred. From report, CrO$_2$ solubility becomes important in this region at high temperature. Main Cr-compound is Cr(OH)$_3$ at pH 7 and around 300 °C on deaerated line. But variation of pH with temperature, the pH value at around 300 °C can correspond to around 1.2 lower value of pH at room temperature and corrosion potential decrease with temperature. By calculation with Nernst equation, corrosion potential at 300 °C decreased compare with room temperature condition. From fig. 2, at pH 7, Ni-oxide and Cr-compound are stable state like as NiO, Cr$_2$O$_3$ and Cr(OH)$_3$ on the deaerated line, and continuous Cr-oxide layer exist on the surface in this region. But over pH 10, Cr-compound changes to soluble state like CrO$_2$.$^{13}$ This change might cause the change of the composition of surface oxide film and the wear damage increase of Alloy 690 in PWRs. The changed water condition can affect metal surface and wear mechanisms. In case of our test results, the dominant state of Cr-compound could be considered with preformed Cr oxide, but more analysis is needed for more positive basis of these changes.

From potentiodynamic test result, fig. 3, at pH 7, corrosion potential of the Alloy 690 was -0.15 V$_{SHE}$ and corrosion current density was $3 \times 10^{-6}$ A/cm$^2$. But, at pH 13.9, corrosion potential was to 0.1 V$_{SHE}$ and corrosion current

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Fig. 1. The relationship of work rate and specific wear rate of Alloy 690 after the fretting test against 409 SS in the pH 7 water and in the pH 13.9 solution at room temperature.

Fig. 2. Pourbaix diagram of (a) Ni, (b) Cr at 288 °C, from report$^{14}$.

Fig. 3. Potentiodynamic test results in NaOH solution.
density increased to $3 \times 10^{-5}$ A/cm$^2$. From calculated value of corrosion potential with Nernst equation was lower than test result. The passive film of Alloy 690 was stable to around 1 V$_{SS}$. In our case, though the corrosion potential had different potential range with literatures, it would be expected that the difference level of oxygen content make the different value of potential level from literatures, the corrosion current density was increased about ten times from at pH 7 to at pH 13.9. It showed that the corrosive wear was far greater at pH 13.9 than at pH 7. From the report, for the corrosive wear, total wear damage is sum of mechanical wear damage and oxide film broken damage. But, at pH 13.9, the passive region was not observed from test result. The composition change of the chromium oxide can have an effect to the oxidation rate of alloy, and more consideration is needed to connect the corrosion test result with wear test results.

3.2 Surface observation

SEM was used to investigate the microstructure of the worn surface. In fig. 4 which shows the worn surface and worn boundary of tested Alloy 690 tube specimen at pH 7, many wear particles were observed. Especially, at the boundary of worn surface and bare metal, the concentration of wear particles was observed. But, at the middle region of worn surface, the worn surfaces consisted of spread thin plates. These thin plates could be considered that wear debris of tube specimen and its counter specimen (409 SS) were agglomerated and spread on the worn surface during wear.

Fig. 6. shows the worn surface observation of Alloy 690 after the wear testing against 409 SS in the pH 13.9 solution at room temperature. From fig. 6.(b), thinner plates were observed than at pH 7 water condition and no debris were observed. At the boundary region of worn surface and bare metal, fig. 6.(d), it hardly observed the boundary. From EDX analysis, differences of chemical compositions were detected as compared with compositions of bare metal. Table. 2 shows chemical composition analysis of worn surface at pH 7 and table 3 shows chemical composition analysis of worn surface at pH 13.9. These results show that compositions of Cr, Ni and Fe were changed. Contents of Cr, Ni and Fe at pH 13.9 were closer to bare metal than that at pH 7. And oxygen content result at pH 13.9 decreased. It would be inferred that the oxide composition on worn surface of Alloy 690 was changed with changed pH, according to the report, and the change of oxide layer affected wear degradation. These results can make up for the corrosion test result at pH 13.9. But more analytical method is needed for more exact analysis.
Fig. 6. Worn surface observation of Alloy 690 after the fretting test against 409 SS in the pH 13.9 solution at room temperature: (a) bare metal in the pH 13.9 solution, \( \times 1000 \), (b) worn surface in the pH 13.9 solution, \( \times 1000 \), (c) worn surface in the pH 13.9 solution, \( \times 200 \), (d) worn boundary in the pH 13.9 solution, \( \times 200 \).

Fig. 7. SEM observation and EDX analysis of the worn surface of Alloy 690 after the fretting test against 409 SS in the pH 13.9 solution at room temperature: (c) bare metal, (d) wear debris particle, (e) surface layer, (f) under the surface layer.

4. Summary

The oscillating wear tests of Alloy 690 on 409 SS were performed at the water chemistry condition and the following conclusions were drawn:

1) From \( 10^5 \) cycles wear test in aqueous solution at room temperature, the wear rate for the material of steam generator tube increased as the work rate increased. And the wear coefficient at pH 13.9 was about ten times greater than that at pH 7. This difference would be originated from the change of the composition of surface oxide film and the wear damage increase of Alloy 600. But more analysis is needed for more positive basis.

2) From the potentiodynamic test results, the corrosion current density of the Alloy 690 increased about ten times from \( 3 \times 10^{-6} \) A/cm\(^2\) at pH 7 to \( 3 \times 10^{-5} \) A/cm\(^2\) at pH 13.9. These results were in proportion to the increased wear coefficient from pH 7 to pH 13.9, and the pH change, from pH 7 to pH 13.9, could be regarded to the increasing factor of wear degradation of Alloy 690 tube.

3) From SEM observation, very thin plates were ob-
served and some debris were observed on the worn surface, especially on the worn boundary at pH 7. Plates at pH 13.9 were thinner than those at pH 7. Through EDX analysis, the change of chemical compositions of worn surface was analyzed. From these changes, the difference of wear damage could be inferred, but more analytical method is needed for more exact analysis.

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