

Oxidation Behavior around PWSCC Crack Tips of Alloy 600

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1. Introduction

Primary water stress corrosion cracking (PWSCC) in reactor pressure vessel head penetration nozzles, their welded parts, and steam generator tubes at pressurized water reactors have been found in many countries [1]. Several models have been reported for the PWSCC phenomena [2,3]. However, the exact failure mechanisms have not been fully understood up to now. It is recognized that systematic approaches to the crack tips using analytic equipment such as TEM and 3DAP are essential to elucidate the PWSCC phenomena. In the present study, the PWSCC cracking properties of Alloy 600 used as the CRDM nozzle material were characterized using microscopic equipment. The microstructural and chemical changes around crack tips during PWSCC were studied using TEM specimens fabricated using a focused ion beam (FIB) method.

2. Methods and Results

2.1 PWSCC experiment

In the test, a 1/2 CT (compact tension) specimen was used. Before the PWSCC test, the CT specimen was fatigue pre-cracked in a length of about 2 mm in the air. The PWSCC test was conducted under the simulated primary water environmental conditions, that is, 1200 ppm B + 2 ppm Li containing pure water at 325 °C, dissolved oxygen content below 5 ppb, a hydrogen partial pressure of 14.3 psi, and an internal pressure of 2300 psi. The maximum stress intensity factor at a crack tip was maintained at 30 MPa√m. Fig. 1 shows a schematic diagram of the loop system for a PWSCC test.

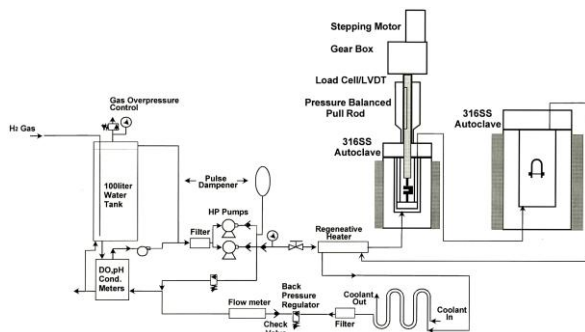


Fig. 1 Schematic diagram of the loop system for a PWSCC test.

2.2 Crack Tip Observation

After the PWSCC test, the cracked CT specimen was used for the OM, SEM/EBSD and TEM/EDS examinations in the plane section. From the results, it was found that the cracks propagated along the random high angle grain boundaries, which had misorientation angles of over 15 degrees between the adjacent grains without any coincidence site lattice (CSL) speciality. It is well known that the random high angle grain boundaries have a higher energy than the low angle and/or CSL special grain boundaries. A TEM image showing the morphology around a crack tip is shown in Fig. 2. The region around a crack tip can be divided into three parts, that is, the crack behind the crack tip, the crack tip itself, and the leading grain boundary ahead of the crack tip. The important results from each part will be briefly described in the next section.

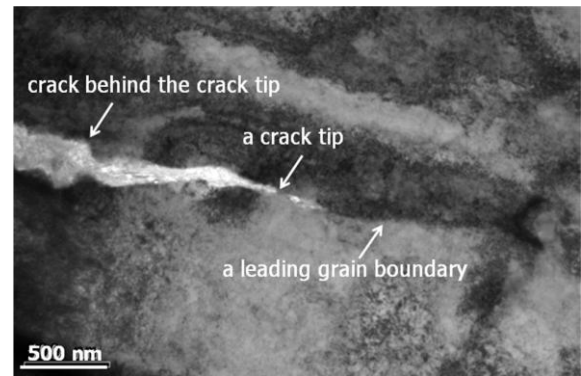


Fig. 2 TEM bright field image showing the morphology around a PWSCC crack tip

2.3 TEM/EDS results

A. Inner crack area behind the crack tip

A bright field image and its related diffraction pattern taken from inside the crack behind the crack tip are provided in Fig. 3. A double layer was formed inside the crack, that is, inner and outer layers during PWSCC. The inner layer, which was adjacent to the matrix, was made of Cr oxides. The outer layer consisted of amorphous what with high O content, needle-type NiO, and faceted (Al,Cr,Fe,Ni) spinels. Moreover, a Ni-rich metal layer (no oxygen and Cr/Fe depletion) existed in the matrix adjacent to the crack wall.

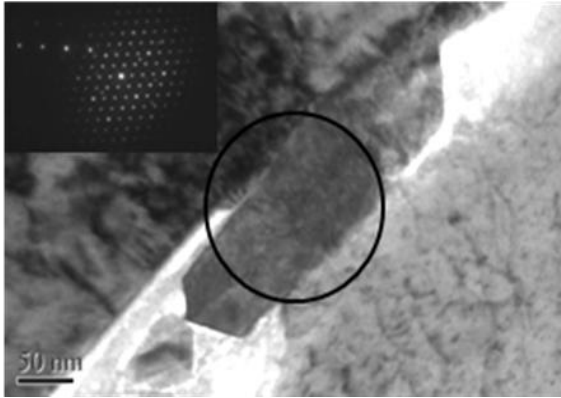


Fig. 3 TEM bright field image and diffraction pattern taken inside a crack

B. At the crack tip

The bright field image taken at the crack tip is shown in Fig. 4. Contrary to the inside of the crack behind the crack tip, only Cr oxides, which were identified as Cr_2O_3 from the chemical composition analysis of the oxides, were found at the crack tip. Cr was depleted on the grain boundary ahead of the crack tip. Since Cr depletion did not occur at the grain boundaries before the PWSCC test, it might be due to the grain boundary diffusion of Cr ions during the Cr oxide formation.

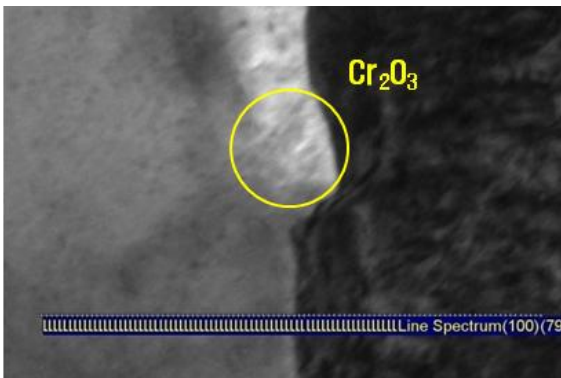


Fig. 4 TEM bright field image taken at the crack tip.

C. On the leading grain boundary

Some discrete Cr oxides were found on the leading grain boundary ahead of the crack tip, as shown in Fig. 5. Ni enrichment (or Cr/Fe depletion) at one side of the matrix, similar with the inside of the crack wall behind the crack tip, occurred at this boundary. Tiny oxides, which were several hundred nano-meters long and are possibly Cr oxides, were found on some leading grain boundaries. Oxygen was detected at the leading grain boundary, and the distance that oxygen diffused along the grain boundary from the crack tip was measured as ~ 700 nm. Most of the phenomena around the crack tips found in the present study agreed well with other's recent results [4-6].



Fig. 5 TEM bright field image taken on the leading grain boundary ahead of the crack tip.

3. Conclusions

Oxygen diffused through a crack from the environment into the grain boundary and its surrounding matrix away from the crack tip. As a result, 1) some Cr oxides were formed in the oxidized (or attacked) grain boundary, and 2) the matrix adjacent to the grain boundary had a lower concentration of Cr, compared with the average value (Cr depletion and/or Ni enrichment).

There was a double oxide layer inside the crack, that is, inner and outer layers. 1) The inner layer, which was adjacent to the matrix, was made of Cr oxides, and 2) the outer layer consisted of (1) amorphous with high O content, (2) needle-type NiO, and (3) faceted (Al,Cr,Fe,Ni) spinels. However, only Cr oxides were found at the crack tip.

The grain boundary diffusion of oxygen through the crack and the resultant metallurgical changes around the crack tip are thought to be significant factors affecting the PWSCC mechanism (crack initiation/growth), and supports the fact that the internal oxidation model is valid to some extent as a PWSCC mechanism in this alloy.

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