Stress corrosion cracking of Ni-base alloys in PWR primary water environment

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1. Introduction

In-service cracking at the Alloy 600 penetration nozzles and surrounding welds in a pressurized water reactor (PWR) has been found after long-term operation. Alloy 182 is widely used as a weld material to join Alloy 600 with stainless steel and/or low alloy steel. It is now well established that Alloys 600 and 182 are susceptible to stress corrosion cracking (SCC) in PWR primary water, which is known as primary water SCC (PWSCC). The cracking of Alloys 600 and 182 was identified as intergranular SCC (IGSCC) [1,2]. Alloy 690, another Ni-based alloy, has been replacing Alloy 600, and Alloy 152 weld metal has also been used to join Alloy 690 instead of Alloy 182. Alloys 690 and 152 are more resistant to PWSCC than Alloys 600 and 182 owing to their higher Cr contents.

The aim of the present study is to investigate the PWSCC resistances of Alloys 182 and 152 by measuring the crack growth rate (CGR) using a compact tension (CT) specimen in simulated PWR primary water. Surface oxidation tests are also conducted under identical conditions to obtain clues to understand the cracking phenomena. The cracking and surface oxidation characteristics are examined using microscopic equipment. Finally, the different PWSCC characteristics of the test welds are discussed in terms of cracking and surface oxidation behavior.

2. Experimental

A mill annealed Alloy 600 round bar was cut in half, and an 80 mm wide × 40 mm deep trapezoidal groove was made in the bar. The groove was filled with the Alloy 182 filler metal by multi-pass submerged arc welding. A similar process was applied to create an Alloy 690/152 weld. The 1/2T CT specimens for PWSCC test were taken from the welded parts. The test was conducted under simulated PWR primary water, that is, 1200 ppm B + 2 ppm Li in pure water at 325 ℃, a dissolved oxygen content below 5 ppb, a hydrogen concentration of 30 $cm^3/kg\ H_2O$. The variation in the crack length of the specimen during the test was measured using the in-situ direct current potential drop (DCPD) method [3], and the stress intensity factor at the crack tip was maintained at 30 MPa√m. A surface oxidation test was conducted in the same environments for 3,600 hours.

After the PWSCC test, the CGR specimen was fractured to examine the fracture surface. The specimens for the optical microscopy (OM) and scanning electron microscopy (SEM) were prepared by chemical etching in a solution of 2 vol% bromine + 98 vol% methanol. The TEM specimens containing PWSCC crack tips or surface oxidation layers were prepared by focused ion beam (FIB) milling. An SEM examination was conducted using a JEOL 6300 (operating voltage 20 kV). A scanning TEM (STEM) analysis was carried out with a JEOL JEM-2100F (operating voltage 200 kV) equipped with an Energy dispersive spectroscopy (EDS) and an Oxford Instruments X-max80T Silicon Drift Detector and an AZTEC analysis system (Ver. 3.1b).

3. Results and discussion

The average CGRs of Alloys 182 and 152 were 1.0×10^{-7} mm/s and 2.4×10^{-9} mm/s at K = 30 MPa√m, respectively. This result confirms that the resistance to PWSCC of Alloy 152 is much higher than that of Alloy 182. The crack propagation outcome in the Alloy 182 weld is shown in Fig. 1(a). As shown in the figure, the crack propagated along a grain boundary, which means that the cracking mode is clearly IGSCC. Fig. 1(b) shows the crack propagation in the Alloy 152 weld. Unlike that in Alloy 182, the primary crack propagated in a mixed (IG+transgranular) mode. This behavior is quite different from that of Alloy 182, in which the cracks propagate along grain boundaries.

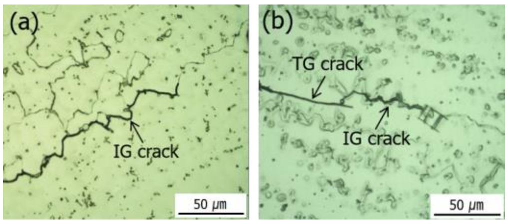

Fig. 1. OM images of (a) Alloy 182 and (b) Alloy 152 welds showing cracking properties.

Fig. 2 shows a STEM image and EDS spectrum images of O, Cr, Ni, Fe and Mn obtained using the Kα1 lines in the Alloy 182 weld. A grain boundary is visible in the STEM image. The most intriguing feature in Fig. 2 is that oxygen diffused down along the grain boundary (dotted circle in the spectrum images), causing the grain boundary to be oxidized.

On the oxidized grain boundaries, Cr was enriched and Cr oxides formed (dotted rectangles in the spectrum images). However, Ni and Mn were depleted in the oxidized grain boundary compared to the average concentration of the matrix.

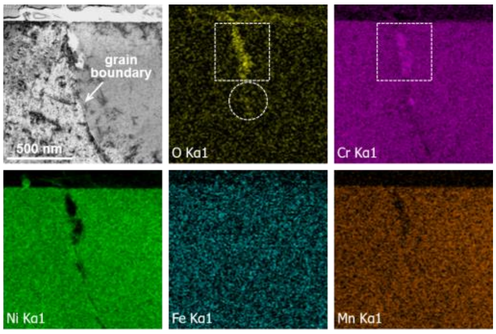

Fig. 2. STEM image, and EDS spectrum images of O, Cr, Ni, Fe and Mn taken from the Alloy 182 weld.

Fig. 3 shows a STEM image and EDS spectrum images of O, Cr, Ni, Fe and Mn obtained using the Kα1 lines in the Alloy 152 weld metal. The most noticeable fact is that oxygen did not diffuse into the grain boundary (dotted circle in the spectrum images). Other intriguing findings are that Cr was depleted and Ni was enriched (dotted circle the in spectrum images), in contrast to the Alloy 182 weld. From these results, it can be confirmed that the surface oxidation phenomena of the Alloy 152 weld was quite different from those of the Alloy 182 weld. The main reason for this difference is thought to be the different chemical compositions, especially the different Cr contents in these two alloys.

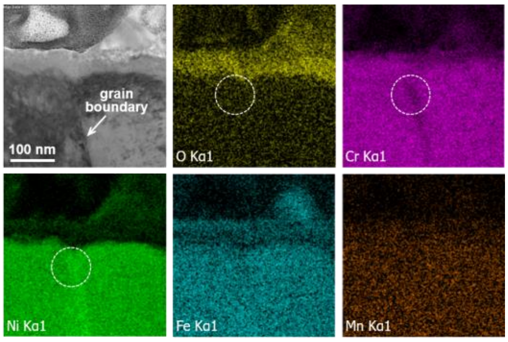

Fig. 3. STEM image, and EDS spectrum images of O, Cr, Ni, Fe and Mn taken from the Alloy 152 weld

The major finding in the current study is that there was a noticeable difference in the IG oxidation behavior between Alloys 182 and 152. Oxygen diffused into the grain boundary in Alloy 182 (Fig. 2), but IG oxidation did not occur in the Alloy 152 weld (Fig. 3). When IG oxidation occurs, embrittlement of the grain boundaries is known to take place, leading to IG ruptures during SCC tests. Fujii et al. [4] showed that an IG fracture readily occurred even under a small amount of applied stress when the grain boundaries were attacked by a pre-oxidization treatment. The lack of IG oxidation in the Alloy 152 weld can partly explain why it has high resistance to PWSCC, because crack propagation can be very rapid when IG cracking occurs. It can also demonstrate why Alloy 152 shows mixed cracking (Fig. 1(b)), instead of IG cracking such as Alloy 182 (Fig. 1(a)). The different IG oxidation behavior in Alloys 182 and 152 appears to lead to the different cracking resistance, and the different cracking modes as well.

4. Conclusions

From the CGR tests, it was confirmed that the resistance to PWSCC of Alloy 152 weld was much higher than that of Alloy 182 weld. Oxygen diffused into along the grain boundaries of Alloy 182 from the outer environment, causing IG oxidation. As a result of the oxygen diffusion, Cr oxide formed in the oxidized grain boundary. These changes in the grain boundary can lower the strength of that grain boundary and therefore increase the level of sensitivity to PWSCC when stress is applied. IG oxidation and the resultant embrittlement of the grain boundaries are believed to be significant factors related to the occurrence of IG cracking in Alloy 182. Oxygen was, however, not detected in the grain boundaries of the Alloy 152 weld. This finding implies that oxygen diffusion along the grain boundaries is significantly suppressed in Alloy 152 welds. Consequently, the IG oxidation behavior was revealed to be closely correlated with the known SCC properties of the two alloys.

References

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