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Intergranular oxidation of Ni-based Alloy 600 in a simulated PWR primary water environment

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ABSTRACT

Oxidation testing of Alloy 600 was conducted in PWR simulated primary water to obtain a clear understanding of intergranular cracking. The degree of intergranular oxidation was highly dependent on the grain boundary character. Random high-angle grain boundaries were deeply oxidized, and nanocrystalline Cr_2O_3 oxides formed. However, oxygen diffusion was significantly suppressed on special boundaries. Metallic Ni was segregated as pure Ni nodules, indicating that the selective oxidation of Cr preferentially occurred. Intergranular oxidation and the resultant embrittlement of the grain boundaries are believed to be major factors affecting the occurrence of intergranular cracking in this alloy.

1. Introduction

Primary water stress corrosion cracking (PWSCC) of Ni-based Alloy 600 (Ni-16Cr-8Fe in wt%) has been a challenging issue given its effects on the primary sides of pressurized water reactors (PWRs) [1]. Despite the fact that a number of laboratory studies have been performed and that several models have been proposed and reviewed to explain the PWSCC phenomenon [2–6], the exact failure mechanisms involved are still not well understood. Although it appears that one single and simple theory cannot explain the entire spectrum of the PWSCC phenomenon, currently there is growing evidence to support intergranular oxidation [7,8], in which oxygen diffusion into the grain boundaries can increase the degree of susceptibility to PWSCC. As a result, intergranular oxidation is responsible for grain boundary embrittlement and therefore, has a major contribution on intergranular stress corrosion cracking (IGSCC). Scott and Calver [5] proposed that IGSCC could occur in a manner similar to internal oxidation. Internal oxidation is essentially similar to the high-temperature oxidation phenomenon that occurs in alloys in which an oxidant diffuses into the matrix and reacts with less noble (more reactive) alloying elements to form discrete oxides [9]. As the temperature decreases, the relative importance of grain boundary diffusion increases, and intergranular oxidation prevails.

Experimental results have clearly shown that cracks initiate at the surface grain boundaries [10] and that they propagate along the grain boundaries [11,12] in Alloy 600 in PWR primary water. Given that PWSCC is linked to IGSCC in most cases, it appears that understanding the corrosion behavior of the grain boundaries is crucial in terms of PWSCC. Recently, numerous studies mainly based on scanning electron microscopy (SEM), transmission electron microscopy (TEM) equipped with energy dispersive X-ray spectroscopy (EDS), secondary ion mass spectroscopy (SIMS), atom probe tomography (APT) and other methods have identified numerous characteristics of intergranular oxidation, including the formation of oxide films and alterations occurring in the underlying metal [7,8,13–19].

Grain boundaries act as an enhanced diffusion path for oxygen, and the intergranular oxidation of Alloy 600 by exposure to primary water is known to be detrimental to grain boundary cohesion [15,16,20,21]. The crack initiation time is significantly reduced [15], and the proportion of cracked grain boundaries increases [16] when specimens are pre-exposed in a simulated PWR environment, even in the absence of applied stress. Changes in the grain boundary structure and chemistry due to oxygen penetration can increase the sensitivity to PWSCC under a load because intergranular oxidization significantly weakens the strength of the grain boundary

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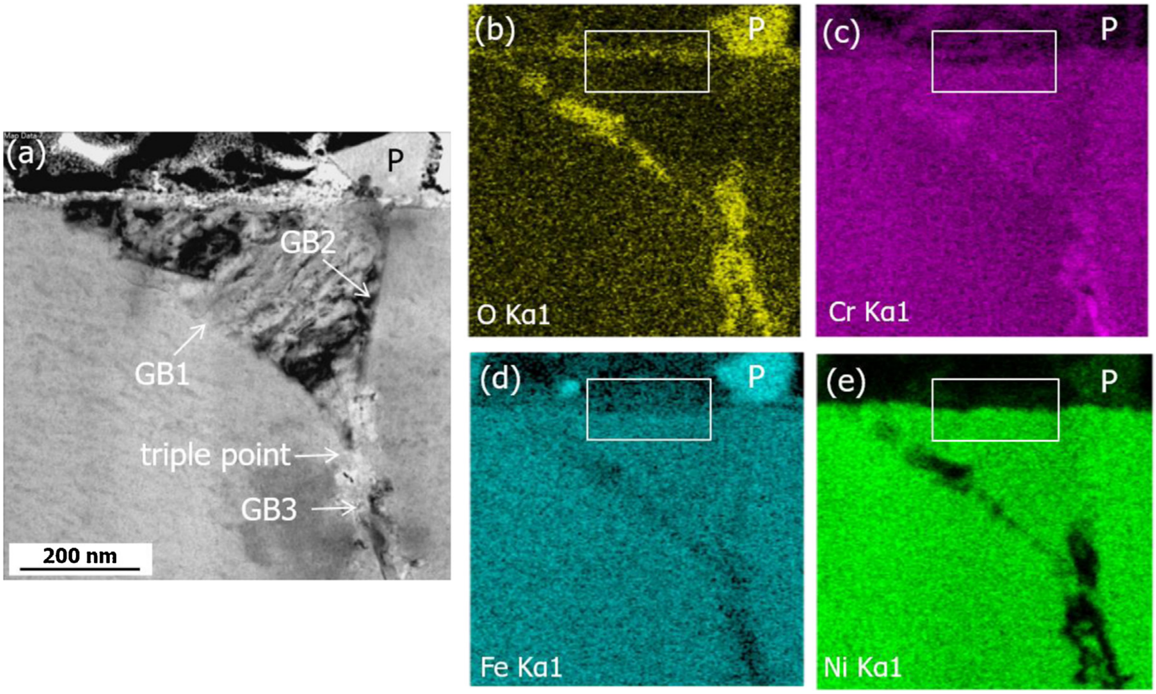

Fig. 1. (a) STEM image of the oxidized grain boundaries, and (b)–(e) EDS spectrum images of O, Cr, Fe and Ni.

itself [20] or the interface between the oxidized grain boundary and the matrix [21]. Therefore, the oxidation process at the metal surface can be the point of crack initiation, and intergranular cracking can be triggered when the depth of intergranular oxidation exceeds a critical value that depends on the applied stress and the strength of the oxidized grain boundary.

Even though many studies have recently reported on intergranular oxidation of Alloy 600, there is a lack of direct experimental evidence on how oxygen diffusion affects the grain boundary change which induces intergranular cracking. Therefore, the aim of the present study was to analyze the intergranular oxidation phenomenon systematically to obtain a clear understanding of intergranular cracking in Alloy 600 by a thorough examination of the alterations in the grain boundary when it is exposed to primary water which simulates the normal operating conditions of a PWR. The formation of nano-scale oxides and chemical alterations at the grain boundaries due to oxygen diffusion were precisely characterized using a variety of microstructural analysis techniques such as SEM, TEM, high-resolution TEM (HRTEM) imaging, and fine-probe chemical analysis in the scanning TEM (STEM) mode. Because the grain boundary character can significantly affect the degree of intergranular oxidation, their roles with regard to intergranular oxidation susceptibility were also investigated. Finally, possible correlations between intergranular oxidation and intergranular cracking in this alloy are discussed based on the observed results.

2. Experimental procedures

A mill-annealed Alloy 600 round bar with an outside diameter of 120 mm, finally heat-treated at 950 °C for 3 h, was used in this study. The composition of the alloy is given in Table 1.

Table 1
Chemical composition of Alloy 600 (wt%).

Ni	Cr	Fe	C	Mn	Ti	Nb	Si	Al	S	P
75.44	16.06	6.66	0.06	0.68	0.21	N.D.	0.03	0.19	0.001	0.014

Coupons with the dimensions of 10 mm × 10 mm × 2 mm were taken from the round bar for an oxidation test. Because the properties of the oxide layer and intergranular oxidation can be sensitive to the surface state of the specimen under testing [22,23], all specimens were polished down using 0.3 μm alumina powders in the same way before being immersed in an autoclave to minimize the surface damage layers formed by the grinding and to ensure identical surface states of all of the specimens.

An oxidation test was conducted in a loop at 325 °C for 3600 h under a typical PWR operating condition which was as follows; 1200 ppm B (weight) as H_3BO_3 and 2 ppm Li (weight) as LiOH in pure water, a dissolved oxygen content of less than 5 ppb, a hydrogen content of 30 cm^3/kg H_2O and an internal pressure of 15.86 MPa.

The oxidized specimens were investigated using various types of microscopes. The specimens for optical microscopy and SEM were prepared by chemical etching in a solution of 2 vol% bromine +98 vol% methanol. The SEM examinations were done with the JEOL 5200 (operating voltage 25 kV) and JEOL 6300 (operating voltage 20 kV). TEM foils containing surface oxidation layers and grain boundaries were prepared with focused ion beam (FIB) milling using a dual-beam Hitachi FIB-2100 system with a Ga^+ incident beam energy of 30 kV and a current of 1–5 nA. To eliminate the deformed surface layers generated from the sputtering of high-energy Ga ions, subsequent ion milling was done with Ar ions with an incident beam energy level of 300 V at an incidence angle of 10° for 10 min.

A STEM/EDS analysis was carried out with the JEOL JEM-2100F (operating voltage 200 kV) equipped with an Oxford Instruments X-max80T Silicon Drift Detector (SDD) with a solid angle of 0.2361 sr and an AZTEC analysis system (Ver. 3.1b). The STEM probe size was approximately 1 nm. EDS spectrum imaging was conducted with a dwell time per pixel of 43.9 ms, an energy per channel of 20 eV, and a process time of 16 μs. A modified Cliff–Lorimer method was used for the quantification of the EDS point analysis. Typically, the standard deviation of the error in the measurement ranged from 2 to 6 percent of the measured value. The peaks of the Cr Lα line (0.50 KeV) and the oxygen K line (0.52 KeV) are closely located