



Effect of dissolved hydrogen on corrosion of Inconel Alloy 600 in high temperature hydrogenated water

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ARTICLE INFO

Article history:

Received 4 May 2011

Received in revised form 7 July 2011

Accepted 8 July 2011

Available online 19 July 2011

Keywords:

Alloy 600

High temperature water

Dissolved hydrogen

Corrosion

Oxide film

ABSTRACT

Electronic property, microstructure and chemical composition of oxide films formed on Alloy 600 in high temperature water with various dissolved hydrogen (DH) levels that allow the Ni/NiO phase transition to occur were studied by employing electrochemical and exposure experiments. The results showed that increasing DH in water decreased the thickness and the ionic defect transport resistance of the oxide film, in conjunction with the increase of Cr- but decrease of Ni-concentrations in the oxide film. Further, it was found that DH weakened the stability and protectability of the Ni spinel oxide film. The DH effect was attributed to the oxidative dissolution process of Ni following the reduction of Ni in the oxide by H₂, indicating the selective dissolution of Ni in the oxide plays an important role in the corrosion of Ni-base alloys in high temperature hydrogenated water. Implications of the results of this work for mechanism of stress corrosion cracking in Ni-base alloys in high temperature hydrogenated water were discussed.

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1. Introduction

It is well known that hydrogen in aqueous solution can be beneficial to metals by reducing the oxidizing species, decreasing the corrosion potential and the oxidation rate, etc. Therefore, hydrogen is often added to high temperature water to maintain low levels of dissolved oxygen (DO) and thereby minimize the corrosion of structural metals. The hydrogen water chemistry has been proved to be a valid technique to mitigate the intergranular stress corrosion cracking (SCC) problems for operating boiling water reactors (BWRs) [1]. Nevertheless, the dissolved hydrogen (DH) can be detrimental to the SCC performance of Ni-base alloys (e.g., Alloys 600, 182 and X-750, etc.) in the primary water of pressurized water reactors (PWRs) [2–8]. Research revealed that a peak in SCC growth and a shortest period in SCC initiation with respect to DH existed in proximity to a key phase transition, the Ni to Ni oxide (NiO) phase transition. It was identified that the DH dependence of SCC was fundamentally described by the extent that the alloy's corrosion potential deviated from the potential of the Ni/NiO phase transition. Not only in primary water, but also in pure water at high temperatures research revealed that the SCC of Ni-base alloys followed a similar DH dependence [7,8]. The concentrations of B and Li in water and water pH had minimal effect on SCC of Ni-base alloys [7,8].

To date, several mechanisms like slip-dissolution/oxidation, hydrogen-assisted cracking and internal oxidation, have been proposed to describe the SCC of Ni-base alloys in high temperature water [9,10]. To attain a better understanding of the SCC mechanism, the composition and microstructure of the oxide film formed on Alloys 600 and 690 in primary water have been analyzed using scanning electron microscope (SEM), transmission electron microscope (TEM), X-ray diffraction (XRD), and atomic force microscope (AFM) [11–17]. Many of these investigations indicated that the oxide was made up of three layers: (1) an internal, a few nm thick layer of Cr₂O₃, (2) an intermediate layer of a spinel-type, Cr-rich oxide containing both Ni and Fe. The protective character of this layer has not been known yet, and (3) an external layer made of discrete Ni-ferrite particles. However, some investigations did not find the internal layer of Cr₂O₃. Instead, they found that the oxide consisted of a continuous Cr-rich (NiCr₂O₄) inner layer which was covered by discrete Fe-rich (NiFe₂O₄) spinel [16,17].

One of the main interests of the investigations of SCC in Ni-base alloys in hydrogenated water is about the mechanism of the DH effect. The peak of SCC growth rate in the proximity of the Ni/NiO transition is expected to be characterized primarily by the influence of DH on both the thermodynamics and kinetics of the corrosion. While the DH effect on the corrosion thermodynamics can be understood easily since the electrochemical potential (ECP) is controlled by DH, the effect of DH on the corrosion kinetics remains poorly understood. Combrade et al. [14] found that the oxide film formed on Alloy 600 in 360 °C primary water exhibited the maximum thickness in the proximity of the Ni/NiO transition

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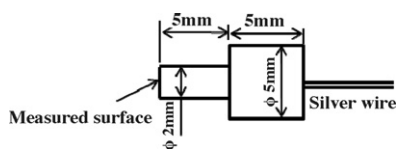


Fig. 1. Schematic drawing showing the geometry and dimension of the specimen used for the CER and electrochemical impedance measurements.

with the lowest Cr content and a less protective character. Terachi et al. [16], however, showed that in 320 °C primary water, the Cr–Ni–Fe spinel layer in the oxide film on Alloy 600 exhibited a minimum thickness at DH = 2.75 ppm. The thickness of the spinel layer further increased when DH reached 4 ppm. Further, they concluded that the SCC susceptibility might have a maximum at the DH corresponding to the NiO/spinel oxide boundary.

Discrepancies on the results for DH effect indicate the importance of further investigations to attain a better understanding of the role of DH. Further, little attention has been paid on the role of the main alloying element, Ni in the corrosion kinetics. It is suggested by the internal-oxidation mechanism that the selective oxidation of Cr plays a key role in SCC. In addition, the corrosion kinetics is not only dependent on the chemical composition and microstructure, but also dependent on the electronic property of the oxide film. To date, systematic studies on electronic properties of the oxide film formed on Alloy 600 in high temperature water are limited. The relationship between the structure, chemical composition and electronic property of the oxide film in high temperature water, which is crucial to the stability and protectability of the film, is still a matter of considerable debate.

The objective of this study is to investigate the DH effect on the corrosion kinetics of Alloy 600 to develop the understanding of the mechanism of the DH effects on corrosion and SCC of Ni-base alloys in high temperature hydrogenated water. Electronic property, microstructure and composition of oxide films formed on Alloy 600 in high temperature water with various DH levels that were above and below the Ni/NiO phase transition were studied by employing electrochemical and exposure experiments. Alloy 600 was selected for the study because it is used extensively in PWRs and is susceptible to SCC. The electrochemical experiments include a combination of in situ electrochemical techniques, i.e. dc electric resistance measurement by contact electric resistance (CER) technique and ac electrochemical impedance measurement by electrochemical impedance spectroscopy (EIS). The exposure tests were conducted by exposing coupons of Alloy 600 in the test environment. Morphology, microstructure and composition of the oxide film formed on the coupon were analyzed.

2. Experimental

2.1. Specimens

All specimens used for the electrochemical and exposure experiments were fabricated from mill-annealed Alloy 600 with a chemical composition (wt%): 0.07 C, 0.37 Mn, 9.46 Fe, 0.34 Si, 0.20 Cu, 15.41 Cr and 74.15 Ni. For the CER and electrochemical impedance measurements, as shown in Fig. 1, a pair of 2-mm diameter, cylindrical specimens with flat surfaces polished by emery papers up to 4000 grit were used. 20 mm × 10 mm × 1 mm coupons were used for the exposure experiments. These coupons were ground using emery papers up to 2000 grit, and then polished by 1- μ m diamond paste. All specimens were cleaned ultrasonically using methanol and pure water before installing them into an autoclave loop for the experiments.

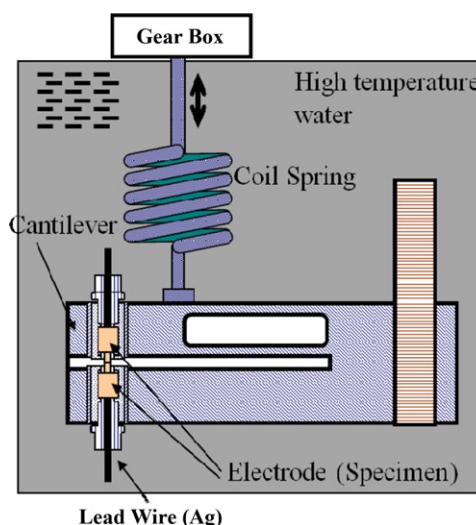


Fig. 2. Schematic drawing showing the setup of the pair of specimens used for the CER and electrochemical impedance measurements in high temperature water.

2.2. Autoclave loop

A low flow rate (100 mL/min) refreshed autoclave loop attached to a CER measurement system was used for both the electrochemical and exposure experiments in high-purity water. The high-purity water was used to isolate the DH effect and to reduce the deposition of soluble oxides on the sample surface. The purity of water in the loop was controlled by using ultra-high purity ($\sim 0.055 \mu\text{S/cm}$) water in the water tank and by purifying the effluent water from the autoclave with an ion-exchanger before flowing back into the tank. DO and DH in the inlet water were controlled by bubbling either pure nitrogen gas, pure hydrogen gas or a mixture of nitrogen and hydrogen gases in the water tank until equilibration reached. Before ramping the autoclave to high temperature, the water tank was N_2 gas bubbled to deoxygenate the inlet water to <10 ppb DO. Then the autoclave was heated up to 80 °C and kept for 1 day while the N_2 gas bubbling of the water tank was continuing. This process was employed to remove oxygen and contaminants in the loop. DO and conductivity of both inlet and outlet water and DH of inlet water were continuously monitored during the test. Since the test aims to clarify the effect of DH, DO was controlled at <10 ppb for all tests.

2.3. CER and electrochemical impedance measurements

The principle of CER measurements and the experimental setup are given in Refs. [18–20]. The electric resistance across a solid–solid contact between two specimens exposed to the test environment is measured by passing a known direct current and monitoring the voltage drop. The surfaces of the two specimens are periodically contacted and disconnected at a desired time intervals for the CER measurements and oxidation of the specimen surfaces. The specimens can be brought into contact by accurate movement of a stepper motor–spring assembly. A schematic drawing showing the setup of the pair of the specimens is shown in Fig. 2.

The dependence of CER on DH was measured in pure water with various DH levels at 288 °C. One of the main interests in varying the DH was to change the ECP, which determines whether the specimen surface is in the Ni regime, NiO regime or at the Ni/NiO transition. The DH at Ni/NiO transition can be estimated according to an equation given in Ref. [7]:

$$C_H = 10^{(0.0111 \times T - 2.59)} \quad (1)$$

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