The Influence of Dissolved Oxygen Concentration on the Corrosion Resistance of 316L Stainless Steel under Simulated BWR Primary Circuit Water Environment

Wan-Wan WANG1,a, Ke-Xin LIANG2,b, Xiang-Jian Li3,c, Yu TAN4,d*

1,2,4 School of Environment Science and Engineering, North China Electric Power University, Baoding, 071003, China
3Hongyanhe Nuclear Plant, Dalian, 116300, China

15230270552@163.com, b kexin91802@163.com, c xiangjiancool@126.com, d lucifertan@163.com

*Corresponding author

Keywords: BWR, Oxide Film, Potentiodynamic Polarization, Mott-Schottky Plot, Dissolved Oxygen.

Abstract. Austenitic stainless steels have been widely applied in the primary circuit of BWR. However, the corrosion caused serious damage to the equipment, affecting the service life of the plant, and lead to many security and economic danger. The oxide film generating on metal surface can slow down the corrosion rate in certain water chemical environment. Researches have shown that the concentration of dissolved oxygen is one of the important factors that affect corrosion resistance of the oxide film. This issue by simulating BWR primary circuit operating mode and controlling the concentration of dissolved oxygen in water solution, studied the corrosion of stainless steel in the autoclave to evaluate the effects of dissolved oxygen on corrosion. Experiments with 316L stainless steel as raw material, after forming an oxide film corrosion experiment, potentiodynamic scanning method and Mott-Schottky plot method were employed to discuss the performance of the stainless steel surface oxidation film. The potentiodynamic polarization curve results indicated that under the dissolved oxygen concentration of 0.28 mg/L and 8.20 mg/L, their current densities of oxidation film were close and significantly less than 0.50 mg/L. Mott-Schottky plot results indicated that under the dissolved oxygen of 8.20 mg/L the carrier concentration of oxide film was the lowest and the corrosion resistance remained its best performance.

Introduction

The neutron moderator and coolant of BWR is boiling water and BWR produces saturated steam within the reactor pressure vessel directly [5]. BWR uses the low concentration of uranium-235 as fuel and must be shut down for refueling. Currently, there were 92 seats BWR in the world, total electric power of 824.31 million kilowatts, accounting for 23% of the total power plants all over the world. Four BWR were being built, with a total installed capacity of 4.63 million kilowatts.

With rapid development of modern industry, the world's energy consumption is growing. Nearly for one hundred years, world energy consumption has increased 20 times. So far, organic fuels such as oil, coal and natural gas account for 85% of the world's total energy consumption. But they are limited in the earth. Organic fuel as very valuable chemical raw materials, playing an important role in the development of the national economy, is only used as a fuel, which is very wasteful. The use of nuclear energy will be the important means to mitigate this problem [1,2]. With rich resources, it is available and accessible to nuclear power, and power generation cost is much lower than the fuel [3,4].

Boiling water reactor primary circuit adopted direct cycle, where the water generated boiling steam within the core and drove turbine to generate electricity outside the heap. Boiling water reactor uses open cycle, so its water chemical system is different from pressurized water reactor. It uses neutral oxygen water system, water oxygen irradiation equilibrium value of about 200~400ppb. Water chemical control of boiling water reactor is to prevent corrosion of materials, to ensure the integrity of
the equipment and to reduce the irradiation dose [6,7]. Boiling water reactor primary circuit uses austenitic stainless steel as material which is most sensitive to intergranular stress corrosion (IGSCC) and IGSCC mainly happen in the weld heat affected zone. Although the intergranular stress corrosion is not an important problem to the safety of boiling water reactor [8], but poses a threat to feasibility and economy of boiling water reactor. In order to reduce the intergranular stress corrosion, it is necessary to make the electrochemical potential (ECP) of reactor structural materials fall to below -230 mV (SHE). So the dissolved oxygen (DO) content must be reduced [9,10]. It can be used to inject nitrogen into feed water, the injection of nitrogen made oxygen content decrease rapidly [11], so as to the intergranular stress corrosion were suppressed.

Experiment

1. 316L stainless steel is prepared, cutting by wire cutting machine into 3*10*12mm samples, with SiC sandpaper mechanical polishing step by step to 2000 mesh. Then the samples were mirror polished with 0.5 um Al2O3 and cleaned with ethanol ultrasonic and high purity water for standby in the oven.

2. The samples were put into a 1L autoclave. In simulated boiling water reactor water working condition of 288 °C / 7.2 MPa, the samples were corroded 120 h (5days) in high temperature aqueous solution [12]. There were 500ppm H3BO3 (as counted by B), 2.2ppm LiOH, 200ppb Co2+ [13] in the solution. High pressure nitrogen was drummed into the autoclave to reduce the dissolved oxygen concentration. The dissolved oxygen instrument was used to monitor the concentration of dissolved oxygen.

3. Electrochemical analysis [14,15] were carried out under atmospheric pressure in a 0.5L electrolytic cell. Support solution was pH 8.4 boric acid buffer solution (0.15mol·L-1 H3BO3+0.0375mol·L-1 Na2B4O7∙10H2O). Samples were encapsulated exposed 0.28cm2 working area by PTFE tape and were set up by the sample frame on the fixed position in the electrolytic cell. The saturated calomel electrode (SCE) connecting salt bridge was as the reference electrode, platinum electrode as auxiliary electrode. Before experiment, high purity N2 was drummed into support solution 1h to remove the dissolved oxygen in solution. A potentiostat (Parstat2273, Princeton) recorded the three electrode system potentiodynamic polarization [16] and Mott-Schottky [17] test results. Mott-Schottky was tested in the above solution, the disturbance voltage of 10 mV, frequency of 1000Hz, the step voltage of 20 mV.

Material composition as follows in Table 1:

<table>
<thead>
<tr>
<th>Material</th>
<th>C</th>
<th>Si</th>
<th>Mn</th>
<th>P</th>
<th>S</th>
<th>Ni</th>
<th>Cr</th>
<th>Mo</th>
</tr>
</thead>
<tbody>
<tr>
<td>316L stainless steel</td>
<td>0.0209</td>
<td>0.4176</td>
<td>0.9780</td>
<td>0.0399</td>
<td>&lt;0.002</td>
<td>10.44</td>
<td>16.82</td>
<td>1.803</td>
</tr>
</tbody>
</table>

The experimental Results and Analysis

Potentiodynamic Scanning

Potentiodynamic scanning curves of three groups of samples were shown in Fig. 1 and the scanning speed was 1 mV/s. In the high temperature solution, the concentration of dissolved oxygen significantly influenced corrosion current density of oxide film generating on stainless steel. Under the dissolved oxygen concentration of 0.28 mg/L and 8.20 mg/L, their current densities of oxidation film were similar and they were significantly less than 0.50 mg/L. It can be inferred that when the dissolved oxygen content was moderate, the protectiveness of the generated oxide film was poorer than high dissolved oxygen and low dissolved oxygen.
The samples of three groups were Mott-Schottky scanned from -1.0V to 1.0V. Mott-Schottky plot was shown in Fig. 2.

Mott-Schottky plot analysis can attain semiconductor type (n or p type) of passivation film, donor concentration $N_D$, acceptor concentrations $N_A$ and flatband potential $E_{fb}$ and so on.

Carrier concentration reflects concentration of electrons or holes in the passivation film/oxide film. The greater the carrier concentration, the better the electrical conductivity of 316L stainless steel, that is the worse the corrosion resistance of passivation film. At a certain potential, the Fermi energy lies at the same energy as the solution redox potential. There is no net transfer of charge, and hence there is no band bending. This potential is therefore referred to as the flatband potential, $E_{fb}$.

Electrochemistry of Semiconductors [18] pointed out that for n type semiconductor, if $E > E_{fb}$, it is the depletion layer; if $E < E_{fb}$, it is the accumulation layer (applied potential $E$). For p type semiconductor, they were just the converse. The non-linear fitting method to analyze the measured M-S plots of bipolar passive films [19] pointed out that from the electronic view points, the inner layer behaves as n-type semiconductor, while the outer layer shows p type semiconductive character. Due to the diffusion of electrons toward p-type semiconductor region and the diffusion of holes toward n-type semiconductor region, a p-n junction will form at the interface between the p-type and n-type semiconductor region. This type bipolar passive film acts as ionic current rectifier, and will block the anodic ion transport across the film and prevent the anodic metal corrosion. Furthermore, the negative fixed charge in the outermost layer prevents aggressive anions from incorporating into the film and enhances the corrosion resistivity. The $C^{-2}-E$ plot indicates that the curve feature of the p-n junction is similar to that of n-type semiconductor; the plots of them both have the positive slopes. So the n type semiconductor parts were investigated in this paper.

N-type semiconductor and p-type semiconductor space capacitance change with potential expression as follows:

For n-type semiconductor:
\[
\frac{1}{C_{sc}^2} = \frac{2}{\varepsilon_0 e N_p A^2} (E - E_{fb} - \frac{K_0 T}{e}) \tag{1}
\]

For p-type semiconductor:
\[
\frac{1}{C_{sc}^2} = -\frac{2}{\varepsilon_0 e N_A A^2} (E - E_{fb} - \frac{K_0 T}{e}) \tag{2}
\]

\(C_{sc}\)—capacitance of the space charge region
\(\varepsilon_0\)—permittivity of free space (8.85419×10^{-14} \text{F/cm})
\(\varepsilon\)—dielectric constant of the semiconductor (15.6) \cite{20}
\(N_D\)—donor density (cm^{-3})
\(N_A\)—acceptor density (cm^{-3})
\(A\)—sample area (cm^{2})
\(E\)—applied potential (V)
\(E_{fb}\)—flatband potential (V)
\(K\)—the Boltzmann constant (1.38×10^{-23} \text{J/K})
\(T\)—absolute temperature (K)
\(e\)—electronic power (1.602189×10^{-19} \text{C})

As shown in Fig. 2, \(K_1, K_2, K_3\) were slope and \(E_{fb1}, E_{fb2}, E_{fb3}\) were intercept of tangents of three groups.

According to the formula of n-type semiconductor \cite{21} and \(k = \frac{2}{\varepsilon_0 e N_p A^2}\), the carrier concentration and flatband potential of different samples can be calculated as listed in Table 2.

<table>
<thead>
<tr>
<th>Dissolved oxygen concentration [mg/L]</th>
<th>Carrier concentration (N_D) [cm^{-3}]</th>
<th>Flatband potential (E_{fb}) [V]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.28</td>
<td>1.98×10^{18}</td>
<td>-1.46</td>
</tr>
<tr>
<td>0.50</td>
<td>4.59×10^{18}</td>
<td>-1.49</td>
</tr>
<tr>
<td>8.20</td>
<td>2.56×10^{12}</td>
<td>-1.38</td>
</tr>
</tbody>
</table>
From Table 2 we can know, for the same materials in high temperature water with different dissolved oxygen levels, the semiconductor properties of oxide film had large differences. In the potentiodynamic scanning performance, two groups of samples (0.28 mg/L, 8.20 mg/L) are similar to each other but the carrier concentrations have obvious gap \(10^6\). The donor concentration of the latter is far less than the former, and the defects in its surface oxidation film are less, meanwhile, in solution, its electric heterosexual attracting capacity is not enough. Under the condition of medium dissolved oxygen concentration, it can get the highest carrier concentration, the most defects in the oxide film, the worst of corrosion resistance. This is consistent with the results showed in potentiodynamic scanning test.

Summary

By simulating BWR primary circuit water conditions, the paper obtained 316L stainless steel oxide film under the condition of different dissolved oxygen concentration. The electrochemical tests indicated that corrosion resistance of oxide film under the condition of high concentration of dissolved oxygen and low concentration of dissolved oxygen were better than moderate concentration of dissolved oxygen. Semiconductor properties of oxide film were tested under the condition of different dissolved oxygen concentration. Under the condition of high dissolved oxygen, oxidation film carrier concentration was lower and the defects were less as well as protectiveness of oxide film was better. Analyze the correlation of the dissolved oxygen concentration and oxide film semiconductor properties can provide a theoretical basis for oxygen enrichment membrane and lean oxygen operation.

References


[10] Zhanpeng Lu, Tetsuo Shoji, Yoichi Takeda, Yuzuru Ito, Akira Kai, Seiya Yamazaki, Transient


[18] Adrian W. Bott, Electrochemistry of Semiconductors.

