

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

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**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 fell 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 Al<sub>2</sub>O<sub>3</sub> 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 H<sub>3</sub>BO<sub>3</sub> (as counted by B), 2.2ppm LiOH, 200ppb Co<sup>2+</sup> [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<sup>-1</sup> H<sub>3</sub>BO<sub>3</sub>+0.0375mol·L<sup>-1</sup> Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub>·10H<sub>2</sub>O). Samples were encapsulated exposed 0.28cm<sup>2</sup> 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 N<sub>2</sub> 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:

Tab.1 Composition of 316L stainless steel

Material	C	Si	Mn	P	S	Ni	Cr	Mo
316L stainless steel	0.0209	0.4176	0.9780	0.0399	<0.002	10.44	16.82	1.803

## 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.

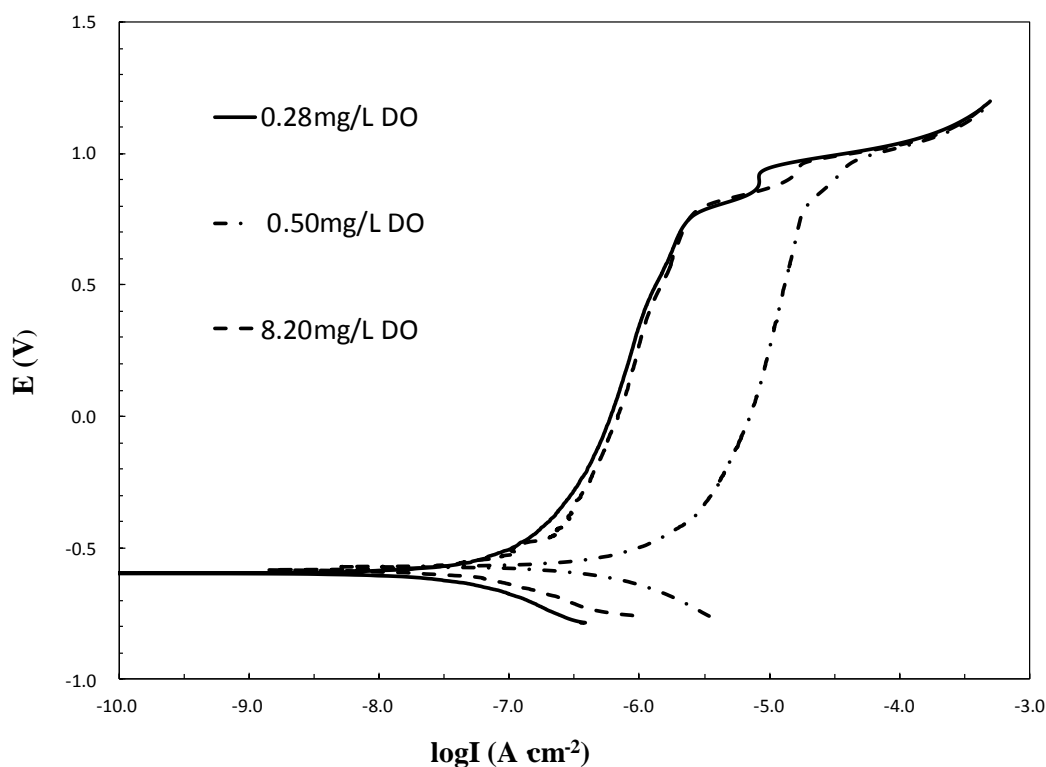


Fig. 1 Potentiodynamic polarization curves

### Mott-Schottky Plot

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  $C^{-2} \sim E$  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:

$$\frac{1}{C_{sc}^2} = \frac{2}{\epsilon\epsilon_0 e N_D A^2} \left( E - E_{fb} - \frac{K_0 T}{e} \right) \quad (1)$$

For p-type semiconductor:

$$\frac{1}{C_{sc}^2} = -\frac{2}{\epsilon\epsilon_0 e N_A A^2} \left( E - E_{fb} - \frac{K_0 T}{e} \right) \quad (2)$$

$C_{sc}$ —capacitance of the space charge region

$\epsilon_0$ —permittivity of free space ( $8.85419 \times 10^{-14}$  F/cm)

$\epsilon$ —dielectric constant of the semiconductor (15.6) [20]

$N_D$ —donor density ( $\text{cm}^{-3}$ )

$N_A$ —acceptor density ( $\text{cm}^{-3}$ )

$A$ —sample area ( $\text{cm}^2$ )

$E$ —applied potential (V)

$E_{fb}$ —flatband potential (V)

$K$ —the Boltzmann constant ( $1.38 \times 10^{-23}$  J/K)

$T$ —absolute temperature (K)

$e$ —electronic power ( $1.602189 \times 10^{-19}$  C)

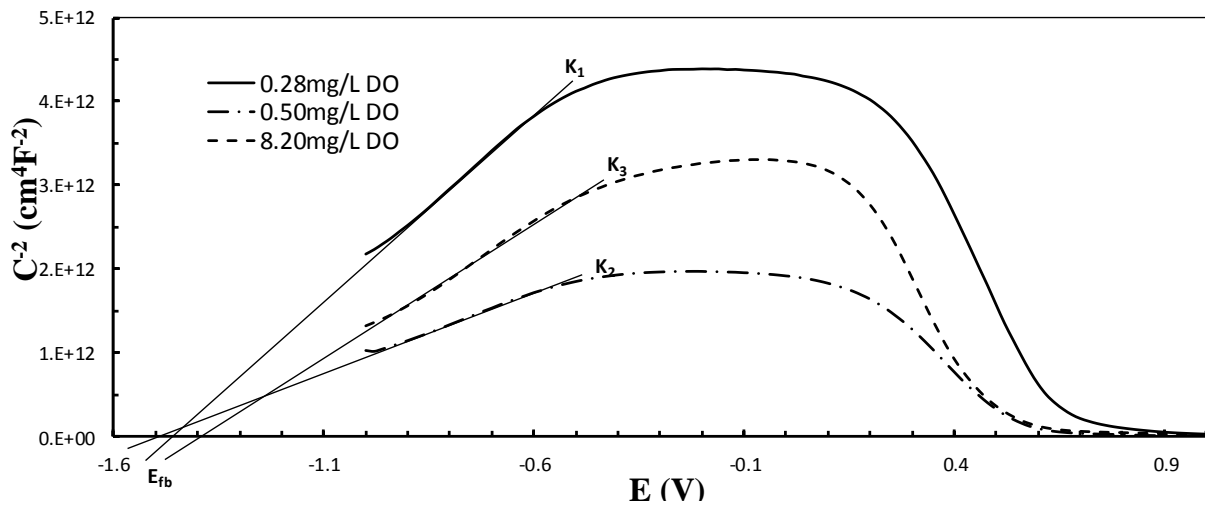


Fig. 2 Mott-Schottky curve

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 [21] and  $k = \frac{2}{\epsilon\epsilon_0 N_D A^2}$ , the carrier concentration and flatband potential of different samples can be calculated as listed in Table 2.

Tab. 2 Calculation results

Dissolved oxygen concentration [mg/L]	Carrier concentration $N_D$ [ $\text{cm}^{-3}$ ]	Flatband potential $E_{fb}$ [V]
0.28	$1.98 \times 10^{18}$	-1.46
0.50	$4.59 \times 10^{18}$	-1.49
8.20	$2.56 \times 10^{12}$	-1.38

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

- [1]Shenghan Zhang, Li Jia, Yu Tan, The influence of  $Zn^{2+}$  on the semiconductor properties of 304L stainless steel passivation film, *Journal of Materials Protection*. 42 (2009) 11-13.
- [2]N.E. Hakiki, Comparative study of structural and semiconducting properties of passive films and thermally grown oxides on AISI 304 stainless steel, *Corrosion Science*. 53 (2011) 2688-2699.
- [3]Dazhong Chen, *Water engineering of nuclear power plant*, China Electric Power Press, 2008.
- [4]Xuezhen Li, The research of the development of China's current nuclear power situation, *Industry and Technology Forum*. 16 (2013) 132-133.
- [5]Minxin He, Attaches great importance to the introduction of boiling water reactor nuclear power plants, *Energy*. 3 (1985) 35-44.
- [6]Guanhua Chen, *Chemical encyclopedia nuclear power technology-computer technology*, Chemical Industry Press. 7 (1994) 8.
- [7]The national development and reform commission high-tech industrial company-the Chinese materials research society, *China's new materials industry development report 2009*, Chemical Industry Press. 15 (2010) 22.
- [8]Maolong Liu, Erkan, Nejd, Yuki Ishiwatari, Koji Okamoto, Passive depressurization accident management strategy for boiling water reactors. *Nuclear Engineering and Design*. 284 (2015) 176-184.
- [9]Z. Lu, T. Shoji, Y. Takeda, Y. Ito, A. Kai, S. Yamazaki, Memory effects and steady state growth kinetics for stress corrosion cracking of a cold worked 316L stainless steel in high temperature pure water, in: *13th International Conference on Environmental Degradation of Material in Nuclear Power Systems*, 2007.
- [10]Zhanpeng Lu, Tetsuo Shoji, Yoichi Takeda, Yuzuru Ito, Akira Kai, Seiya Yamazaki, Transient

and steady state crack growth kinetics for stress corrosion cracking of a cold worked 316L stainless steel in oxygenated pure water at different temperatures, *Corrosion Science*. 50 (2008) 561-575.

[11]S. Roychowdhury, V. Kain, R.C. Prasad, Effect of nitrogen content in sensitised austenitic stainless steel on the crack growth rate in simulated BWR environment, *Journal of Nuclear Materials*. 410 (2011) 59-68.

[12]Stellwag B, The mechanism of oxide film formation on austenitic stainless steels in high temperature water, *Corrosion Science*. 40 (1998) 337-370.

[13]Alamr A, Bahr DF, Michael Jacroux, Effect of Alloy and Solution Chemistry on the Fracture of Passive Film on Austenitic Stainless Steel, *Corrosion Science*. 46 (2006) 925-936.

[14]Fengping Wang, Wanli Kang, Hemin Jing, *Corrosion electrochemical theory, method and application*, Chemical Industry Press, 2008.

[15]ZhengJia, Changsong Dai, Ling Chen, *Electrochemical measurement methods*, Chemical Industry Press, 2010.

[16]Sanchez-Tovar, Leiva-Garcia, Garcia-Anton, Characterization of thermal oxide films formed on a duplex stainless steel by means of confocal-Raman microscopy and electrochemical techniques. *Thin Solid Films*. 576 (2015) 1-10.

[17]M. BenSalah, R. Sabot, E.Triki, L. Dhouibi, Ph. Refait, M. Jeannin, Passivity of Sanicro28 (UNS N-08028) stainless steel in polluted phosphoric acid at different temperatures studied by electrochemical impedance spectroscopy and Mott–Schottkyanalysis. 86 (2014) 61-70.

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

[19]Ruijing Jiang, Changfeng Chen, ShuqiZheng, The non-linear fitting method to analyze the measured M-S plots of bipolar passive films, *Electrochimica Acta*. 55 (2010) 2498-2504.

[20]Yang Jiao, The influence of  $Zn^{2+}$  on the corrosion resistance of zirconium alloy cladding material in PWR primary circuit, BaoDing: North China Electric Power University, 2012.

[21]V. Stehr, J. Pfister, R. F. Fink, B. Engels, and C. Deibel, First-principles calculations of anisotropic charge-carrier mobilities in organic semiconductor crystals, *Web of Science*. 83 (2011) 11-13.