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Electrochemical behaviour of 316L stainless steel exposed to representative chemistry in pressurised water reactors under proton radiation

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ABSTRACT

The electrochemical behaviour of 316L stainless steel has been investigated in representative primary PWR environment under proton irradiation. The electrochemical potential of 316L stainless steel and the environmental parameters (temperature, hydrogen pressure, etc.) have been measured continuously under irradiation. Highly reproductive electrochemical results have been observed with fast increases of the potentials under irradiation. This oxidative response increases with increasing flux and decreases with increasing hydrogen pressure. Depending on the temperature, the oxidative response can either be reduced or enhanced. Moreover, the synergetic effect of thermal ageing and cumulated fluence on 316L stainless steel can influence the electrochemical potential with or without irradiation.

1. Introduction

In Pressurised Water Reactors (PWR) activated corrosion products in the primary circuit can cause material degradation in the reactor core eventually leading to the shutdown of nuclear reactors. The most common localised corrosion process is stress corrosion cracking (SCC) which can produce material failure by cracking [1–3]. In the presence of an aggressive environment (radiation, radiolytic products, impurities like chloride, ...), the general or localised corrosion process can be accelerated causing materials such as austenitic stainless steel, traditionally regarded as corrosion resistant, to be affected by the corrosion process [4–9]. This is the reason that the study of radiolysis effect on the materials used inside the reactors becomes so important.

In general, the reaction of water radiolysis can be written as Eq. (1). Due to the ionizing radiation, the radiolysis of water produces: hydrated electrons, $H^{\cdot}$ atoms, $HO^{\cdot}$ and $HO_2^{\cdot}$ radicals, H_3O^+ and OH^- ions, H_2 (dihydrogen) and H_2O_2 (hydrogen peroxide) molecules. The global equation of water radiolysis is now well understood experimentally as well as theoretically [10–14].

$$H_2O \xrightarrow{Ionizing\ radiation} e^-_{aq},\ H^{\cdot},\ HO^{\cdot},\ HO_2^{\cdot},\ H_3O^+,\ OH^-,\ H_2,\ H_2\ O_2 \quad (1)$$

The radiolytic yield, noted as $g(X)$, is used to quantify the water radiolysis and is defined as the quantity of the X compound (i.e. $H^{\cdot}, HO^{\cdot}, HO_2^{\cdot}, H_3O^+, OH^-, H_2, H_2O_2$ ...) created for 100 eV deposited energy. Unit for the radiolytic yield is mol J^{-1} which equals to 9.646×10^6 molecules for 100 eV. The Linear Energy Transfer (LET) is the deposited or transferred energy in the media. The LET of incident radiation, as the dose rate, can significantly change the values of primary radiolytic yields. In short and generally, the yields radical products ($H^{\cdot}$, $HO^{\cdot}$, $HO_2^{\cdot}$ ...) decrease with the increase of LET while the molecular yields (H_2, H_2O_2, ...) increase.

In the primary circuit of a PWR, water radiolysis occurs at high temperature (HT), 280–320 °C, and high pressure (HP), 15.5 MPa. The products of water radiolysis can modify the corrosion issues of some materials, such as the internal components made of austenitic stainless steel (304L and 316L mainly) [15–17]. The presence of radiolytic products may change the PWR water environment into an oxidative environment and thus accelerate the corrosion process. Therefore, in order to minimise the occurrence of water radiolysis, hydrogen is added into PWRs. It is proven that with the addition of hydrogen (25–50 cc/kg (STP)) radiolysis can be inhibited for bulk water [18–20]; however there is very little experimental date at high temperature and high pressure proving this theory valid for interface under PWR operational conditions.

Electrochemical corrosion potential (ECP) measurement may be used to predict the evolution of SCC occurred in nuclear reactors.

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Based on results obtained for Boiling Water Reactors (BWRs), it is assumed that an ECP < −230 mV (SHE) can achieve SCC mitigation. Due to the absence of dissolved oxygen in PWRs and the presence of some hydrogen, reducing conditions are expected in PWR primary circuits. However, it has been pointed out that zero dissolved oxygen does not necessarily mean the ECP is less than −230 mV (SHE) [21]. Concerning Irradiated Assisted Stress Corrosion Cracking (IASCC), Macdonald et al. [22] and Urquidi-Macdonald et al. [23] have shown that with the increasing concentration of H_2, ECP will be shifted to a more negative value: even with low concentration of H_2, the ECP is lower than −230 mV (SHE) in PWR primary conditions. On the other hand, according to Ishigure et al. [24], ECP can be increased importantly in BWR hydrogen water chemistry conditions depending on factors as dose rate, flow rate and water chemistry. So, ECP measurement under proton irradiation has been chosen as the main approach to study the 316 stainless steel in representative primary PWR chemistry in order to get a better understanding of the corrosion issues inside the PWRs.

The proton beam is chosen in the present approach to control the production of radiolytic species because it can be considered as representative of neutron irradiation induced effects in primary coolant circuit of PWRs.

2. Materials and methods

2.1. Experimental setup

A specific working cell, so-called HTHP (stands for high temperature and high pressure) cell, is designed to record the free corrosion potential of the 316L stainless steel in PWR water chemistry under irradiation, as illustrated in Fig. 1. The front part of the HTHP cell is linked to the beams which first arrive at the 316L stainless steel, penetrate through and then diffuse in the PWR water. The middle part of the cell is the tank which contains the PWR water. It is made of a zirconium alloy which has been oxidised in air at 500 °C in order to develop an electrical isolation layer of ZrO_2. The volume of the tank is approximately 20–25 ml. The heating devices with the help of 6 cartridge heaters inserted surrounding the tank can quickly change the temperature of the cell. The tank is closed with the target material, 316L stainless steel, which is maintained straight inside and sealed by using two stainless steel seal rings on both surface. A the back part of the HTHP cell, several types of sensors are located (thermocouples, pressure sensors, hydrogen sensor, ...). They are connected to a computer which can record the data in real time. Two platinum wires are served as reference electrodes. Thermocouple, pressure and hydrogen sensors are used to control and record the detail information of the experimental conditions. It needs to be emphasised that all the sensors, especially the platinum wires are located few centimetres away from the irradiation zone in order to avoid the possible direct irradiation effects on them. More detail descriptions of the cell construction has been well explained elsewhere [26,27]. To summarize, the corresponding primary PWR relevant conditions are:

- *PWR water:* containing 1000 ppm boron ([B]), 2 ppm Lithium ([Li]) with dissolved hydrogen and no dissolved oxygen.
- *High temperature:* around 280–300 °C.
- *High pressure:* about 90–100 bar.

The proton beam used in this study is delivered by Cyclotron in CEMHTI (Conditions Extrêmes et Matériaux: Haute Température et Irradiation) laboratory of CNRS Orléans in France. The Cyclotron can provide variable energy with different intensity. In our case, a 23 MeV proton beam is used in order to let the proton beams penetrate the 316L stainless steel disc and irradiate the PWR water, which has been calculated to be about 6 MeV emerging at the 316L/PWR water interface. Concerning the flux, it varies five orders of magnitude from 6.6×10^7 to 6.6×10^{11} H^+ m^{-2} s^{-1} which corresponds intensity from 3 pA to 30 nA. With the calculation of SRIM (*The Stopping and Range of Ions in Matter*), it can be ensured that 100% of the protons penetrate the disc of 316L stainless steel and stop in the PWR water in a distance about 480–500 μm.

2.1.1. 316L Stainless steel

2.1.1.1. Composition. The composition of the 316L stainless steel used in the study is indicated in Table 1. The surface of the disc is prepared first by a mechanical polishing, and followed by a cleaning process. The diameter of the disc is 26 mm while the thickness is about 0.9 mm. The thickness is chosen on one hand to endure the high pressure inside the HTHP cell and on the other

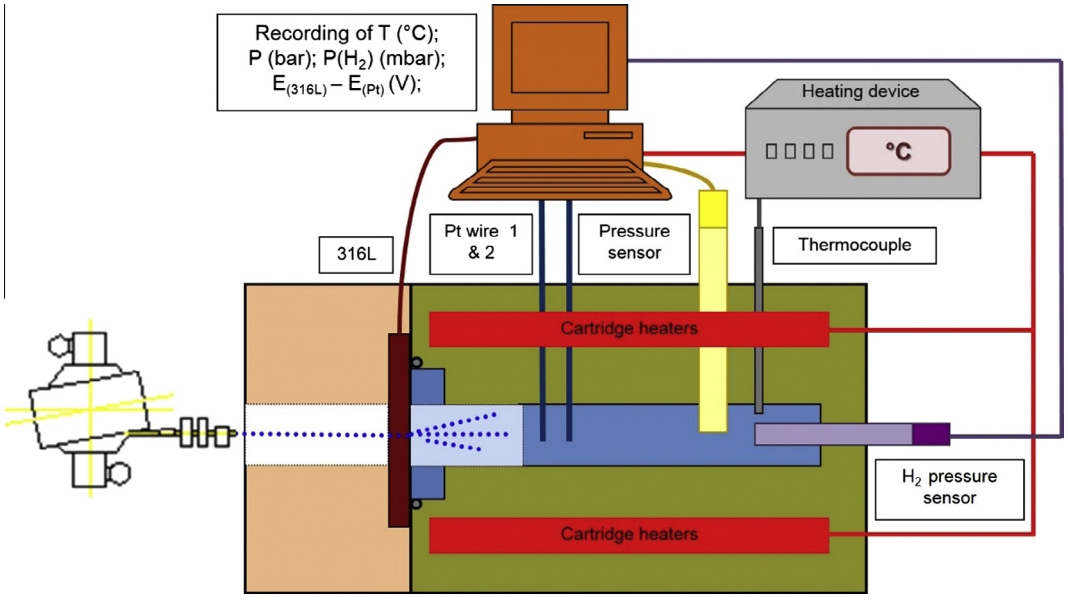

Fig. 1. Schematic layout of high temperature and high pressure (HTHP) electrochemical cell, working at the range [25 °C, 1 bar]–[300 °C, 90 bar].