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Hydrogen evolution rate during the corrosion of stainless steel in supercritical water

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ABSTRACT

The interaction of water with metal surfaces at high temperatures leads to the significant release of hydrogen gas. A systematic investigation of hydrogen evolution from fresh and oxidized stainless steel (SS316) surfaces is carried out in a tubular reactor, at supercritical water conditions. A linear relationship is found between the reactor surface area and the rate of hydrogen gas released. Results show that the evolution of hydrogen gas is a zero-order reaction, with the activation energy of 105.9 kJ mol^{-1} for the oxidized surface.

1. Introduction

Worldwide energy consumption is rapidly increasing and is accelerated by economic development and increasing population. The expected increase in energy demand and the growing awareness of global warming has led to international efforts to develop a new advanced generation of nuclear energy systems. These Generation IV (GEN-IV) proposals include the Supercritical Water-Cooled Reactor (SCWR) as one of the six advanced nuclear reactor concepts under the program. The SCWR is a reactor which uses supercritical water (SCW) as both moderator and coolant. It will generate electricity with an outlet temperature of 625 °C and pressure of 25 MPa, which are much greater than those of existing pressurized water reactors (PWRs) [1]. The SCWR is expected to become one of the principle sources for the large scale production of hydrogen gas.

Since the SCWR operates at higher temperatures and pressures than existing PWRs and fossil fuel plants, the corrosion of structural materials under these extreme conditions, has been identified as a critical problem [2]. The concentrations of dissolved O_2 and H_2 in the coolant, as well as pH, are all crucial parameters affecting the speciation and solubility of the passivation layer formed by the metal oxides and hydroxides that accumulate on the inner surfaces of the SCW bearing components. The high temperatures and pressures make SCW very aggressive in terms of corrosion, particularly in an oxidizing environment. The in-core generation of oxidizing species such as hydrogen peroxide H_2O_2, OH radical, and oxygen, due to the radiolytic breakdown of water, can increase the corrosion of reactor components, as well as have an effect on the transport and deposition of corrosion products [3]. The high dissolved oxygen concentration is a cause of concern for both the general corrosion, and the stress corrosion cracking susceptibility of the structural material in the reactor [4]. Corrosion in the system can cause increased maintenance time, cost, and a loss of power generation [5–7]. In order to minimize the corrosion in the heat transport systems of the PWRs and Boiling Water Reactors (BWRs), hydrogen water chemistry (HWC) is being examined to include the addition of oxygen scavenging species such as hydrogen gas and hydrazine to the coolant [1,8–10], as well as lithium hydroxide [11] for alkalinity control. Hydrazine (N_2H_4) is a strong reducing agent, currently used both in thermal and nuclear power plants because of its ability to eliminate dissolved oxygen effectively, and protect structural materials against corrosion. Power plants with Water-Cooled-Water-Moderated Energy Reactors (VVERs or WWERs) use hydrazine as a source of the hydrogen that is required to suppress the accumulation of the oxidizing species generated by radiolytic processes in the coolant water [9]. However, it is not yet clear whether these strategies will provide adequate chemistry control in the SCWR environment.

Austenitic stainless steels, nickel-based alloys and zirconium alloys are widely used in the design of nuclear power plants and are regarded as possible candidate materials for the water bearing components of the proposed SCWR [12–15]. These materials will be subject to corrosion, particularly in the harsh supercritical water environment at which these next generation designs will operate [15,16]. It is well known that at high temperatures, significant amounts of hydrogen gas can be released during the oxidation of

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a metal surface in the formation of a corrosion layer. In the case of stainless steel, this corrosion product is typically a magnetite/hematite oxide layer on the surface of the metal. Of particular significance to the SCWR is that hydrogen is not only produced during the oxidation of the metal surface, but is also a primary product of the radiolytic breakdown of water in the in-core region of the reactor water loop.

There has been a long history of study in the role of hydrogen and the effect it has on the corrosion rate of a material [17–24]. It is worthwhile mentioning that the presence of excess hydrogen can become a crucial factor in the failure of materials in nuclear power systems. For instance, hydrogen can diffuse into a metal and precipitate as a hydride such as Zr_2H_3 in the case of zirconium alloys [25]. Such absorption of hydrogen can lead to phenomena such as stress corrosion cracking, hydrogen embrittlement, and delayed hydride cracking, which can weaken the structure and contribute to the catastrophic failure of the reactor components [1,14,26–28].

The reactions that take place in the corrosion layer are very similar to those that are currently being investigated for the development of catalytic water splitting cycles intended for large scale hydrogen production. There are several thermochemical water splitting mechanisms under examination involving base metal oxides. For a detailed review of water splitting using various metal oxides, the reader is refereed to Souza [24].

From a viewpoint of a nuclear reactor chemistry control strategy, hydrogen generated in the heat transport system of the SCWR may potentially have a vital role as an oxygen scavenger, effectively removing the corrosive radiolytic products from both the in-core and out-of-core regions. An understanding of how much hydrogen will be produced in the SCWR pressure tube is important in estimating the amounts of other oxygen scavenging compounds, such as hydrazine, which may be added to the coolant for corrosion control.

In our previous work [29], the dissolved hydrogen concentration in the effluent of a tubular stainless steel reactor was found to be rather high at conditions relevant to the operation of the SCWR. In this study, we systematically investigate the effects that the reactor surface area, temperature, pressure, and the residence time of deoxygenated water, have on the rate of hydrogen evolution during corrosion, on both fresh and oxidized stainless steel surfaces. Hydrogen evolution was studied in a flow-through reactor using SS316 tubing with volumetric at pump flow rates ranging from 0.1 to 1.5 mL min^{-1}. Reactor temperatures and pressures ranged from 650 to 750 °C and 5 to 25 MPa, respectively. Once the hydrogen evolution rate had reached a steady state, oxygenated water was introduced into the flow system. An estimate was obtained of how much hydrogen reacts with the dissolved oxygen. The apparent corrosion rate at SCWR flow conditions was also estimated, through the determination of metal loss to the effluent. The metal concentrations in the reactor's effluent were analysed using voltammetry methods, and the concentrations of O_2 and H_2 were continuously monitored by a Dissolved Gas Analyser (DGA).

Molecular dynamics simulations of supercritical water at the iron hydroxide interface were conducted at the temperature of 640 °C for total water densities of 0.044 and 0.055 g cm^{-3}. These densities are similar to those found in the SCWR. Iron hydroxide is the primary corrosion product produced when ferric metals rust at SCW conditions. A corrosion crevice was modelled by confining the water between parallel iron hydroxide surfaces spaced 40 nm apart. Simulations support the experimental findings of greater hydrogen evolution rates at lower densities. Water was found to penetrate into the surface at the lower density configuration, where once within the iron hydroxide structure, catalytic water splitting may occur.

2. Experimental and simulation details

2.1. Apparatus

A stainless steel flow-through reactor was used to produce hydrogen and to examine the hydrogen-water chemistry (HWC) at conditions relevant to the SCWR. A schematic diagram of the experimental set-up is shown in Fig. 1. All parts of the flow-through apparatus were constructed using stainless steel (SS316) and connected using SS316 capillary tubing (OD = 1.59 mm, ID = 0.75 mm) and zero dead volume unions (Valco®). The feed line was connected to three bottles, each containing air saturated, hydrogen saturated or deoxygenated water. This was achieved by sparging with ultrapure air, hydrogen and helium gas (Praxair high purity gases, UHP 5.0), respectively. Low pressure check valves (anti-backflow, Valco®) were installed on the sparging lines just outside the bottles to prevent water backflow from the bottles into the lines. The volumetric flow rate of the water was continuously monitored by weighing a collected volume of water over a set time period. Three separate HPLC pumps (Waters® 590) were used for control of the volumetric flow rates. Pump 1 and 2 were used to control the flow rate of air saturated and hydrogen saturated water respectively. Pump 3 was used to control the flow rate of the deoxygenated water. All three flow channels were combined by using a zero dead volume cross (Valco®) and were connected to a switch. With the switch in position 1, the water flows through the oven/reactor and when the switch is in position 2, the water flows directly through to the DGA for calibration.

Experiments were carried out using SS316 tubing with different internal diameters resulting in varying surface-to-volume ratios, from 7.79 to 53.33 cm^{-1}. Table 1 shows the elemental composition of the tubing. The reactor tube was placed in a custom-made sand bath inside a programmable muffle furnace (Isotemp® 650 Series, Fisher Scientific). Furnace temperature was maintained above the water's critical temperature by the built-in proportional integral derivative (PID) controller equipped with a type K-thermocouple. The effluent exiting the reactor was cooled to ambient temperature using a custom built heat exchanger (length = 2.5 m, made of SS316 tubing), coupled to a cold plate (TE Technology®, Inc.). The temperature of the heat exchanger was maintained by a temperature controller (TC-24-25, TE Technology®), and the pressure in the system was controlled by an adjustable back pressure regulator (P-880, Upchurch). Both the temperature and pressure of the system were monitored and recorded using a data logger (PrTC-210, Omega®). After cooling, the depressurized effluent was then passed through the dissolved gas analyser (SRI Instruments®, 8610C) which was equipped with a helium ionization detector (HID) for the measurement of the gas composition. The dissolved oxygen concentration and pH of the effluent were also monitored, using a NeoFox system (Ocean Optics®) equipped with a FOSPOR oxygen probe and Orion 5 Star metre (Thermo Scientific) respectively.

2.2. Calibration curve for hydrogen analysis

An HPLC pump was used to maintain a steady flow rate of 0.1 mL min^{-1} and the actual flow rate was verified by collecting a volume of water over a set time period. The pump flow rate was adjusted until the desired amount of water was collected, corresponding to the target rate of 0.1 mL min^{-1}. A calibration curve for hydrogen gas was obtained by first feeding hydrogen saturated water with a known hydrogen concentration of 1.6 mg L^{-1} (ppm) into a dissolved gas analyser. The hydrogen gas was separated from the continuously flowing water using concentric tubes, with an outer gas collection tube made of glass, and an inner permeable silicone extraction tube through which the gas was able to effuse,