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Corrosion behavior of alloy 316L stainless steel after exposure to supercritical water at 500 °C for 20,000 h

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ABSTRACT

Oxidation behavior of alloy 316L stainless steel static capsules were investigated by long-term exposure to the supercritical water at 500 °C and 25 MPa for various exposure times. It was found that the thickness and weight gain vs. exposure time followed parabolic law. Elemental and phase analyses indicated that long-term exposure to the SCW resulted in formation of scales identified as Fe_3O_4 (outer layer), Mn-Fe-Ni-Cr spinel (inner layer) on the substrate, and Ni-enrichment (chrome depleted region) in the alloy 316L. Oxidation phenomena and scales grown on the Alloy 316L as the result of long term exposure to the supercritical water was discussed.

1. Introduction

In recent decades, the necessity to develop a new generation of nuclear energy systems has resulted in the development of several concepts for a supercritical water cooled reactor (SCWR) in terms of materials selection and application conditions [1]. Supercritical water reactors are promising generation IV nuclear reactors which provide a much higher thermal efficiency and are simpler to construct than current light water reactors [2]. Based on the working conditions, the operating temperature and pressure of an SCWR are designed to exceed the thermodynamic critical point of water. Supercritical water is a nonpolar solvent that can dissolve gases like oxygen to complete miscibility. Water above a temperature of 374.15 °C (647.15 K) and a pressure of 22.1 MPa is in a supercritical state and acts as a dense gas, exhibiting properties significantly different from that of water below the critical point [3]. The Canadian SCWR [4] will operate at a pressure of 25 MPa, with a core inlet temperature of about 350 °C and core outlet temperature of 625 °C.

Austenitic stainless steel (ASS) tubes are currently being used in the highest temperature areas of super- heaters and reheaters in thermal power boilers [5]. Behnamian et al. [6] reported that ASS contains sufficient chromium element in the composition to allow development of protective chromium rich oxide layer in the form of Cr_2O_3 during oxidation at high temperatures in SCW. However, there are significant differences in the oxidation performance of the various 300 series steels, depending largely on the chromium and nickel concentrations in the steel, although minor elements such as silicon, manganese, titanium, molybdenum, and possibly carbon can also be important in this respect [7]. In general, Cr can promote the formation of a protective surface oxide and Ni can enhance the stability of the protective oxide. Thus, a higher amount of Cr and Ni in the composition of the stainless steel can provide a better high temperature performance of this alloy in SCW.

It is known that in Fe-Ni-Cr alloys, outward diffusion of iron and nickel and reaction with oxygen leads to the formation of oxides such as Fe_3O_4, Fe_2O_3, FeO, and NiO, depending on the oxygen concentration, temperature and exposure time of SCW [6]. The high corrosion resistance of ASS in SCW is attributed to the formation of a protective chromia-based oxide rather than a spinel (FeCr2O4)-based oxide [6]. Goncharov reported that Fe and Cr diffusion coefficients in Cr_2O_3 are quite similar, while Fe diffusion in $FeCr_2O_4$ is 3 times faster than Cr diffusion making these oxides less protective [8]. Additionally, it is observed that presence of other alloying elements (Mn, Al, Ti, Si) can alter the compositions of these oxides or lead to the formation of additional oxide layers [6]. However, these Cr-based passive films are soluble in SCW under oxidizing conditions [9] due to the formation of Cr(VI) species [25]. As the chromium oxide forms on the surface, chromium depletions take place in the steel beneath the originally

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protective scale and lead to the localized cracking of that scale. Afterward, iron from the steel enters the Cr_2O_3 rich layer, transforming it to a spinel structure, and consequently allowing rapid outward transport of iron to form oxides on the outer surface [7]. Based on the oxygen species and the amount of oxygen in the solution, these Cr-based passive films may be soluble in SCW. Thus, the oxidation behavior of the alloy in SCW can vary significantly. Therefore, selecting an alloy which will maintain the integrity of the passivation layer at the SCW conditions, is a crucial requirement in choosing a material for pressure tube lining, fuel cladding and other components exposed to radiation [10,11].

To our knowledge, no study was conducted on the long-term exposure of alloy 316L static capsule exposed to the SCW. In the current work, alloy 316L SS capsule samples will be exposed to the SCW at 500 °C and 25 MPa for various exposure times. The oxidation behavior of alloy 316L will be investigated using weight change, X-ray diffraction (XRD), and scanning electron microscopy (SEM) equipped with energy-dispersive X-ray spectroscopy (EDS). Final remarks will be made with respect to the oxidation phenomena in the applied SCW condition.

2. Experimental methods

2.1. Materials, sample preparation and experimental procedures

Alloy 316L SS tubes with an outer diameter of 9.525 mm and a wall thickness of 1.65 mm were purchased from Swagelok. The chemical composition in weight percent (wt%) of the alloy is given in Table 1. shows the chemical composition in weight percent (wt%) of the alloy used in the present research. The tubes were manufactured according to specifications defined in ASTM-A213 for stainless steels and were supplied in a solution annealed (1 h at 915 °C and then water quench). Fig. 1 shows a scanning ion micrograph of the alloy 316L. Solution treated microstructure with equiaxed grains was observed. The pattern in the micrograph illustrated that cold drawing and post heat treatment resulted in the formation of twins in the microstructure.

Capsule samples were cut into 10 cm long sections to make capsule specimens for SCW exposure. Tube sections were washed with pentane, isopropyl alcohol, and acetone in an ultrasonic bath to degrease completely. Air-saturated neutral pH deionized water with an oxygen concentration of 25 ppb was used for the SCW test. The inlet conductivity of the water was 0.055 µS/cm (Milli-Q® Integral Water Purification System). Two high pressure 316L SS caps were used to make static capsules from tube sections. The static capsules were placed in a Lindberg tube furnace under vacuum condition of 6×10^{-4} mTorr and heated to 500 °C. The temperature of the furnace was calibrated using Nextel ceramic insulated lead wire rated to 815 °C (Omega) as the reference thermocouple. The pressure of the water inside the tube depends on its volume and temperature. Based on the NIST steam chart [12], the pressure of a tube filled with a 9.5% volume of DI water is 25 MPa at 500 °C. Additionally, calibration sample was connected to a pressure monitoring equipment during the corrosion experiment and the pressure remained at 25 ± 1 MPa at 500 °C for 20000 h. Stress on the tube wall due to the internal pressure was calculated by heating separate static capsules to 500 °C.

Table 1
Elemental analysis of the alloy 316L used in the experiments (provided by the supplier).

Alloy	Chemical composition (wt.-%)								
316L stainless steel	Fe	C	Cr	Ni	P	Si	Mo	Mn	S
	balance	0.03	17.2	11.7	0.02	0.8	2.1	2.0	0.03

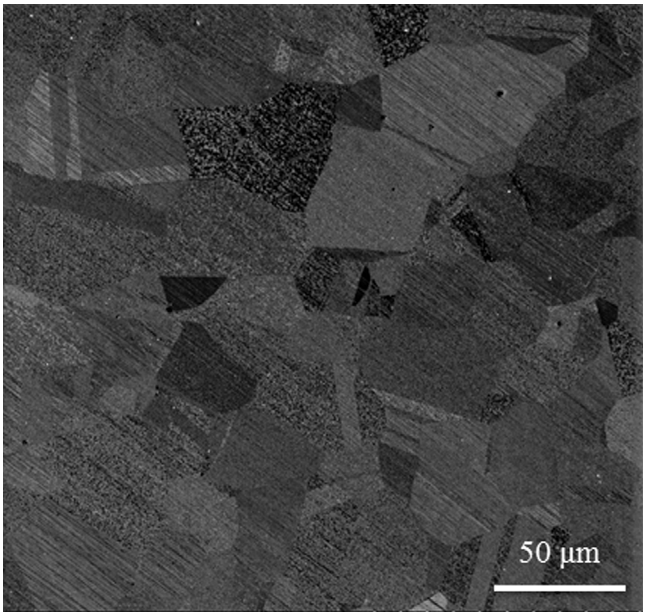

Fig. 1. SEM micrograph of the alloy 316L SS tube sample used in the experiments.

2.2. Analysis equipment

All the samples were weighed using a METTLER-TOLDO XPE105 with an accuracy of 0.01 mg to record the weight change before and after exposure in SCW. To minimize the error in measurements, every weight gain measurement was conducted five times.

After SCW exposure, the capsules were cut into smaller segments. The inner surfaces of the tubes were plated with a thin layer of Ni coating to avoid spallation of the oxide film during sample preparation. Samples were mounted with epoxy resin and polished down to 0.5 µm in alumina solution before metallurgical examination. The surface morphologies of the oxide layers on the inner wall of the tubes were examined with a scanning electron microscope (ZEISS EVO-MA15) equipped with an energy dispersive x-ray spectroscope. Cross-section morphologies were captured with backscattered electrons; a Bruker AXS diffractometer (Bruker Discover 8) operating with Cu-K_α radiation with a wavelength of 1.5405 Å at 40 kV and 40 mA in the 2-theta range 20–80° at a scan rate of 0.05° per second was used for X-ray diffraction (XRD) analysis.

3. Results and discussion

3.1. Phase analysis by XRD

X-ray diffraction pattern analyses were carried out on the alloy 316L stainless steel capsule samples exposed to the SCW at 500 °C and 25 MPa for various exposure times up to 20,000 h to identify different oxide phases and results were illustrated in Fig. 2. Depending on the exposure time, various phases such as magnetite [Fe_3O_4], Fe-Cr spinel [$FeCr_2O_4$], and chromia-based oxide[$(Fe,Cr)_2O_3$] phases were detected in the XRD patterns, with austenite as the main phase known as the main phase in as-received material. The XRD pattern of the capsule sample exposed to the SCW at 500 °C for 500 h illustrated that Fe_3O_4 phase was the major oxide scale formed on the exposed surface of the alloy 316L, with smaller quantities of chromia-based oxides. Similar phases were present when the exposure time was increased to 5000 h, however, the intensity of magnetite rose while the intensity of austenite was reduced. XRD patterns of the alloy 316L SS tube samples taken from capsules exposed to the SCW for 5000 h indicated that the coarse crystallite formed on the tube surface was Fe_3O_4. Chromium oxide and hematite on the inner surface of the alloy 316L SS tube samples were