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Corrosion behavior of pre-oxidized HR-224 superalloy in supercritical water environment at 700 °C

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HIGHLIGHTS

- Pre-oxidized HR-224 provides better corrosion resistance than as-received one.
- $Ni(Cr, Fe)_2O_4$ spinel/Cr_2O_3/α-Al_2O_3 were observed after pre-oxidized treatment.
- Continuous Al_2O_3 layer can effectively decrease outward migration of metal ions.

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ABSTRACT

Corrosion of cladding materials in supercritical water (SCW) environment is a key reliability issue for the safety of nuclear power plant. In this study, we propose to use the pre-oxidized treatment to provide better corrosion resistance of cladding materials in the SCW environment. The nickel-based superalloy HR-224 was first pre-oxidized in flowing air at 982 °C for 100 h to establish a continuous and dense scales and then exposed in the SCW environment with high oxygen content (8.3 ppm) at 700 °C and 24.8 MPa for cyclic oxidation testing up to 1300 h. The pre-oxidized samples exhibit better corrosion resistance than as-received samples in the SCW environment. After pre-oxidizing process, triple scales, $Ni(Cr, Fe)_2O_4$ spinel/Cr_2O_3/α-Al_2O_3 were observed, and the growth of inner α-Al_2O_3 layer is predominant in the SCW environment. The α-Al_2O_3 layer in pre-oxidized samples was found to effectively decrease outward migration of metal ions in Alloy HR-224 and thus provides better corrosion resistance than as-received samples in SCW environment.

1. Introduction

Supercritical Water-cooled Reactor (SCWR) whose operating environment exceeds the critical pressure and temperature of water (22.4 MPa and 374 °C) has been considered as an option to replace light water reactor (LWR) by the Gen-IV Nuclear Energy System International Forum [1]. The main advantages of SCWR over the current LWR include: (1) higher thermal efficiency, (2) more compact thermal component, (3) combination of existing LWR plant and supercritical-pressure (SCP) fossil power plant technologies, and (4) higher safety. However, SCW is a medium with high solvency of most gas, including oxygen [2,3]; thus it is expected that in-core components, such as fuel cladding, in an SCWR is under more aggressively oxidizing environments than current LWRs. According to criteria for cladding materials [4], temperature of fuel cladding can exceed 750 °C during an accident transient. Moreover, due to the radiolysis of water, high concentration of hydrogen peroxide is in the reactor coolant and decomposition of hydrogen peroxide can lead to an increase in dissolved oxygen content. Lin et al. [5] states that the G-value $\{G(e^-_{aq}) + G(H) + G(OH)\}$ in SCW environment is about 28 at 400 °C and 25 Mpa. In addition, Wang et al. [6] indicated that intense radiolysis effects can lead to extremely high concentrations of H_2O_2 and O_2 near the core region and the concentrations of these two oxidizing species were considerably higher than those in BWRs. Therefore, corrosion resistance of fuel cladding materials in high temperature and high oxygen content environments is the key issue for SCWR design. However, most studies were conducted on corrosion behavior of alloys in SCW environments with low oxygen content (~25 ppb) [7–15].

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Forming slow-growing, thermodynamically stable oxide layers has been demonstrated as a useful way to enhance the corrosion resistance of materials. For example, pre-oxidation has been widely used to improve the corrosion resistance of Ni-based superalloys [16] and steels [17] in light water reactor environment. Recently, the oxide layers are found to effectively degrade the diffusion rate of metal and oxygen ions, especially for Cr_2O_3 and Al_2O_3 formed in metallic alloys for high-temperature application. Chromia-forming Austenitic alloys, Alloy 800H [15] and Alloy 625 [18,19], have been shown to be able to form protective Cr-rich spinel oxides in SCW environments under various oxygen contents. Some studies [20–23] also investigated the oxidation behavior of alumina-forming alloys as structural material of SCWR because Al_2O_3 is more thermodynamically stable than Cr_2O_3 at 700 °C [24]. Given that Al_2O_3 possess good corrosion resistance in the corrosive fluid [25,26], the alumina-forming alloys have been reported to provide better long-term protection than general chromia-forming alloys in aggressive SCW environments [27–30]. Recently, Deodeshmukh et al. [31] conducted cyclic oxidation tests on commercial heat-resistance alloys in the flowing air at 982 °C and their results showed that newly developed Alloy HR-224 exhibits better oxidation resistance than other chromia-forming alloys and comparable oxidation resistance to alumina-forming alloy 214 in the flowing air due to formation of continuous alumina scale in HR-224.

In this study, we propose to intentionally use the pre-oxidized treatment to form the passive Al_2O_3 layer to provide better corrosion resistance of cladding materials in the SCW environment. The nickel-based superalloy HR-224 was first pre-oxidized in flowing air at 982 °C for 100 h to establish a continuous and dense α-Al_2O_3 layer. Then the samples were exposed in the SCW environment with high oxygen content (8.3 ppm) at 700 °C and 24.8 MPa for cyclic oxidation testing up to 1300 h. The oxidation characteristic of pre-oxidized Al_2O_3 layer of HR-224 in SCW environment was investigated. The corrosion behavior of pre-oxidized HR-224 was evaluated and compared to as-received samples.

2. Experimental

2.1. Materials

Alloy HR-224, provided by Haynes International, with chemical composition analyzed by inductively coupled plasma-mass spectrometer (ICP-MS, Agilent 7500ce) in weight percentage listed in Table 1 was used in this study. The size of samples is 20 mm × 20 mm with a thickness of ~1 mm. The samples were first polished progressively with fine silicon-carbide abrasive paper to a grit of 2500, and then mechanically polished by diamond finish of 1 μm.

2.2. The pre-oxidation process at high temperature

Pre-oxidation experiments were conducted in an alumina furnace tube with 76 mm in diameter and 500 mm in length. Once the furnace reached 982 °C, polished samples were placed on an alumina holder and inserted into the furnace. Then the furnace was ventilated with nitrogen (2 L/min with purity higher than 99.99%) at least for 10 min to purge residual air in the tube. After the samples reached designated temperature (982 ± 3 °C), the atmosphere was switched to dry air (1 L/min) to complete the 100 h pre-oxidation process.

Table 1
Normal composition of the investigated nickel-based superalloy in wt% analyzed by ICP-MS.

	Al	Ni	Cr	Fe	Mn	Ti	Mo
wt %	3.3	48.7	18.4	28.5	0.3	0.5	0.3

2.3. Corrosion test in SCW environment

Corrosion tests were performed in a dynamic loop system as shown in Ref. [18] for 100 h, 300 h, 600 h, 1000 h and 1300 h. Most parts of the system were made of 316 stainless steel as well as the 0.73-L autoclave and sample holder were composed of Alloy 625, designed to tolerate a maximum pressure of 27.5 MPa. The primary loop system was established for high temperature SCW environments. The samples were exposed under a pressure of 24.8 MPa (3600 psi) in high purity water provided by a high-pressure liquid chromatography (HPLC) pump from a 15 L reservoir tank. The test temperature and water flow rate was controlled at 700 ± 5 °C and 3 mL/min respectively. The secondary loop was used to monitor water chemistry at room temperature. The dissolved oxygen level of water was 8.3 ppm by mass, which was monitored at ambient temperature with a detector Orion 1816 and controlled by introducing argon and oxygen into the water tank in the secondary loop. The conductivity of water near the inlet valve was less than 0.1 μS/cm.

2.4. Post test analysis

After corrosion test, the weight change of the specimens was measured by means of gravimetry (electronic balance: Sartorious CPA255D) with a precision of 0.01 mg. The microstructure evolution of samples was analyzed using both scanning electron microscope (SEM: JEOL JSM-6330 F) at an acceleration voltage of 15 kV, and transmission electron microscope (TEM: JEOL JEM-2010F and JEOL ARM200F) at an acceleration voltage of 200 kV equipped with an energy-dispersive X-ray spectrometer (EDS). The crystal structures of the oxides were characterized using the TEM diffraction patterns. The TEM samples were prepared by mechanical polishing and Ar ion-milling at 3–5 keV by the Gatan Precision Ion Polishing System (PIPS, Model691).

3. Results and discussion

3.1. Oxide structure of alloy HR-224 after pre-oxidized process

Fig. 1 (a) shows the oxidized surface of Alloy HR-224 after 100 h exposed to flowing air at 982 °C. Discrete oxide islands in 50 μm diameter, being close to grain size (58.2 ± 12.6 μm) of Alloy HR-224 were observed on the samples, suggesting that the gap between islands as indicated by arrows in Fig. 1 (a) is grain boundary. Surface oxide was identified as Ni-Fe-Cr rich oxides by EDS analysis. To understand the composition of surface oxides of samples, TEM image and line-scan analysis by EDS were conducted on the cross-section of pre-oxidized samples across the oxide layers, as displayed in Fig. 1(b) and (c). Fig. 1(c) shows the EDS profiles of the locations corresponding to the dashed lines in Fig. 1(b). TEM line-scan profile shows that a distinct boundary appeared between the three layers of the oxide; Ni, Cr, and Fe accumulated in the outer oxide layer and following Cr-rich and Al-rich oxide layers. Furthermore, the results of cross-sectional TEM mapping analysis as shown in Fig. 2 indicates the primary composition elements of outer oxide layer are Fe and Ni. Cr and Al respectively show high intensity in the second and third layer of oxides, suggesting that these two layers are single phase.

To further understand the structure of surface oxides of samples, selected area diffraction (SAD) was conducted in the positions marked as A, B and C in Fig. 1(b) and the results of diffraction