Effect of low oxygen concentration on the oxidation behavior of Ni-based alloys 625 and 825 in supercritical water

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ABSTRACT

In this study, the oxidation behavior of Ni-based alloys 625 and 825 in supercritical water containing 5000 ppm of dissolved oxygen at 500 °C was investigated by scanning electron microscopy coupled with energy-dispersive spectroscopy, X-ray diffraction, and laser Raman spectroscopy. Alloy 625 and 825 showed a pitting-like phenomenon after 500 h of exposure. The structure and composition of the oxides formed on alloy 625 and 825 were similar, namely, an outer layer of Fe oxides, spinel structures, and $Ni(OH)_2$; and an inner NiO layer. The mechanism for the formation of the oxide films was proposed, and the factors affecting corrosion of Ni-based alloys were discussed in detail. In addition, the corrosion resistance performance of alloy 625 and 825 was compared.

1. Introduction

At temperatures and pressure greater than 374.15 °C and 22.1 MPa, respectively, the properties of water will drastically change compared with those at ambient temperature. Supercritical water (SCW) has several anomalous properties, e.g., low density, low dielectric constant, and low ionization constant, because of the remarkably strong hydrogen bonds [1–3]. Hence, in contrast to liquid water, SCW behaves more like a non-polar solvent and dissolves an almost infinite amount of organic compounds and gases.

Supercritical water oxidation (SCWO) is an oxidation process that can efficiently decompose organic matter within a few minutes [4]. After the reaction, carbon in the organics is converted into carbon dioxide, and other atoms such as sulfur, chlorine, and phosphorus are converted into their corresponding salts [3]. Excess oxygen is supplied to ensure the complete decomposition of organics [5,6]. The amount of oxygen is calculated on the basis of the chemical oxygen demand (COD) of the organics undergoing treatment, and the coefficient of oxidation (defined as the proportion of oxygen and COD) ranges from 1.1 for full-scale commercial SCWO plants [7] for 3.0 at laboratory systems [5,8,9]. The presence of salts and oxygen leads to severe corrosion of the candidate materials, i.e., Ni-based alloy and stainless steel. Corrosion problems constitute the major obstacle to the commercialization of SCWO [10,11].

Ni-based alloys have been widely used under harsh conditions in chemical industries and coal-fired and nuclear power plants because of their outstanding corrosion resistance and high strength. For instance, Ni-based alloys 690 and 625 are used to manufacture steam generator tubes and other facilities in pressurized water reactors [12] and supercritical water reactors (SCWRs) [13]. Ni-based alloys 740 and 617 are selected as materials for superheaters and reheaters in ultra-supercritical units in coal-fired systems [14]. In SCWO systems, Ni-based alloys 625, 825, and 800 are also widely employed for manufacturing reactors and heat exchanger pipes.

Several studies have reported the corrosion behavior of Ni-based alloys in SCW with extremely low concentrations of oxygen (less than 8.3 ppm, corresponding to that in nearly pure water environment in SCWRs and ultra-supercritical power plants) [15–21], high concentrations of only oxygen (greater than 10000 ppm) [22,23]; and high concentrations of both oxygen and salt [24,25]. A duplex-layer oxide structure is reportedly formed on the alloy surface, with a Ni-rich and Fe-rich outer oxide layer and a Cr-rich inner oxide layer [15–18,22,24–26].

The concentration of oxygen in SCW environment clearly affects the specific oxide structures and corrosion rates of Ni-based alloys. Tan et al. [27] concluded that NiO formed on the surface of alloy 625 in SCW containing 8.3 ppm of oxygen. Similar results have been reported by Kritzer et al. [23] for the corrosion behavior of alloy 625 in neutral SCW containing oxygen ($[O_2]$ = 46080 ppm). However, with a decrease of in oxygen concentration to 150 ppb, a duplex film structure

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with Ni(Cr,Fe)$_2$O$_4$ and Cr$_2$O$_3$ as the outer and inner layers of alloy 625, respectively, is formed, as reported by Chang et al. [18] From these results, it is apparent that Cr$_2$O$_3$ is the main oxide formed in SCW containing relatively low oxygen content, and the corrosion products are converted into NiO in the presence of high oxygen concentration.

However, few studies have reported the corrosion of Ni-based alloys in SCW containing oxygen at concentrations between 100 ppm and 10000 ppm, which correspond to the that of working fluids passing through reactors, heat exchangers, and their connecting pipes in SCWO systems. This area is defined as "low oxygen concentration area" in SCWO systems. In addition, the specific oxygen concentration at which the phase transition of corrosion product occurs is still unknown. Thus, understanding the corrosion behavior of candidate materials at a low oxygen concentration is crucial for selecting materials and controlling corrosion in SCWO systems.

In this study, the corrosion behavior of Ni-based alloys 625 and 825 at 500 °C, in the presence of 5000 ppm dissolved oxygen (DO), was investigated in detail. After exposure, the morphologies, micro-structure, and chemical composition of the oxide films were analyzed, and the growth mechanism of the oxide film was proposed.

2. Experimental and instrumentations

Ni-based alloys 625 and 825 were supplied by A. Finkl & Son Company. Table 1 summarizes their chemical composition (weight percent). Raw materials were cut into cubic pieces with dimensions of 4 mm × 6 mm × 5 mm by using a laser cutting machine, and a hole was bored into each piece for mounting onto the autoclave. Next, the pieces were polished by using SiC paper. Finally, the coupons were immersed in acetone for 30 min and ultrasonically degreased, and then cleaned with deionized (DI) water. Next, the samples were stored in a vacuum drying box at room temperature to prevent oxidation by oxygen in air. The oxidant was prepared by diluting hydrogen peroxide (H$_2$O$_2$) solutions (30 wt.%, Tianjin Fuchen Chemical Agent Co., Ltd) to the desired concentrations with DI water.

The experiment was conducted on the corrosion test system as de-scribed in our previous study [25,28]. The autoclave in the system composed of Hastelloy C-276, while the other auxiliary facilities were composed of 316 stainless steel. A hot jacket fixed on the autoclave was utilized as the heat source for the system. The temperature signals from the inner space of the reactor and heating jacket were measured and sent to a PID controller to automatically regulate the temperature with a deviation of less than 2 °C. The autoclave and connected pipes were purged by flowing nitrogen gas for 10 min, and all the valves were closed before heating. To eliminate the effect of galvanic corrosion, an insulating rod composed of diamond was used to fix the test specimen.

Table 1
Composition of metal species in Ni-based alloy 625 and 825.

Species	Compositions (wt.%)	
	Alloy 625	Alloy 825
Ni	Bal.	Bal.
Cr	23	23.5
Mo	10	3.5
Nb	4.15	–
Fe	5	31.5
Al	0.4	0.2
Ti	0.4	1.2
Mn	0.5	1.0
Cu	0.5	1.5
C	0.1	0.025
Si	0.5	0.5
P	0.01	–
Si	0.5	–
S	0.015	–
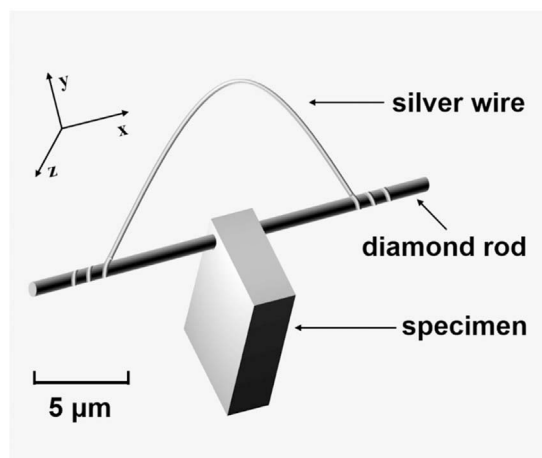
Fig 1. Schematic diagram of a specimen holder.

Table 2
Conditions used for corrosion tests.

Run No.	Sample	Dissolved oxygen (ppm)	Exposure time (h)	Temperature (°C)	Pressure (MPa)
1	Inconel 625	5000	24	500	24
	Incoloy 825	5000	24	500	24
2	Inconel 625	5000	48	500	24
	Incoloy 825	5000	48	500	24
3	Inconel 625	5000	72	500	24
	Incoloy 825	5000	72	500	24
4	Inconel 625	5000	100	500	24
	Incoloy 825	5000	100	500	24
5	Inconel 625	5000	200	500	24
	Incoloy 825	5000	200	500	24
6	Inconel 625	5000	300	500	24
	Incoloy 825	5000	300	500	24
7	Inconel 625	5000	400	500	24
	Incoloy 825	5000	400	500	24
8	Inconel 625	5000	500	500	24
	Incoloy 825	5000	500	500	24

A silver, but not ferric, wire was used to hang the specimen for elim-inating the interference from Fe ion. Fig. 1 shows the schematic of a specimen holder, and Table 2 summarizes the parameters for the cor-rosion experiments. After each run, the coupons were cleaned using acetone and DI water and stored in the vacuum drying box at room temperature.

Scanning electron microscopy (SEM, JSM-6390A, JEOL) coupled with energy-dispersive X-ray spectroscopy (EDS) was employed to ex-amine the morphologies and microstructures of the oxide films. X-ray diffraction (XRD, D/max-Ultima IV, Rigaku) patterns were recorded in the scanning range of 10° to 100° to analyze the composition of the oxide films. Laser Raman spectroscopy (LRS) is a high-precision method for analyzing the material composition, and its results can be utilized to supplement and verify the XRD results. However, LRS is rarely em-ployed to analyze oxide films because it requires prior knowledge about the oxidation behavior of alloys, in order to avoid misinterpretation of the results due to the similar characteristic frequencies of different bonds [29]. In our studies, the oxidation films were tested by LRS using an HR800 (Horiba Jobin Yvon) laser Raman spectrometer with a 633 nm He Ne laser as the excitation source and a laser power of 17 mW. The exposure time was 30 s, and the wavenumber ranged from 100 cm^{-1} to 1500 cm^{-1}. A Kratos AXIS ULTRA electron spectroscopy chemical analysis (ESCA) system was employed to analyze the surface chemistry analysis. After each run, the effluents were detected by spectrophotometry with 1,5-diphenylcarbohydrazide (DPCI) to confirm the presence of Cr (VI).