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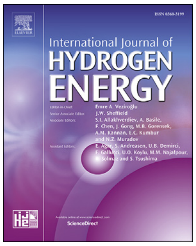

Effect of ammonium chloride on corrosion behavior of Ni-based alloys and stainless steel in supercritical water gasification process

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ABSTRACT

The corrosion behavior of 316 SS and three Ni-based alloys 625, 600 and 800 was evaluated by exposing in SCW at 400 °C and 24 MPa with 6000 ppm NH_4Cl for 70 h. Various of analytical techniques were used for corrosion analysis. 316 SS underwent severe corrosion attack for general corrosion, pitting corrosion and intergranular attack. Inconel 625 showed the best corrosion resistance in the test environment. Fe oxides and spinel were identified by XRD on all of the SCW-exposed samples. Trace amounts of NiO was also identified on the surface of samples, however, Ni was selectively dissolved and depleted in oxide films, and nickel ammine may form at the relatively low temperature during the heating and cooling process.

Introduction

Concerning about both the global warming and energy security, hydrogen has become one of the most promising energy to replace fossil fuels. However, there are few efficient ways for hydrogen production by now. When the temperature and pressure of water reached to its critical point (374 °C, 22.1 MPa), water undergoes significant changes on its solvent properties and transport properties. Supercritical water gasification (SCWG) is a new hydrogen-producing technology which was raised by Modell [1] in 1970s. In a SCWG process, organic materials (including biomass, coal, etc) were heated to elevated temperature and reacted with supercritical water, forming light gases. Due to the strong organic solubility in supercritical water, a SCWG process is able to completely dissolve the organic matters in biomass, forming high density and low viscosity liquid which can be gasified at high temperature and pressure, and subsequently forming mixed gases containing large proportion of hydrogen.

Due to the extreme operate conditions (high temperature, high pressure and complex materials containing various corrosive ions), corrosion behavior of candidate materials of SCWG plants should be deeply understood. For the reason that the operate temperature of SCWG is generally above 600 °C, Ni-based alloys and stainless steel are widely chosen as the

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construction materials for heat exchangers and reactors in SCWG systems. Nickel based alloys are commonly used as construction materials for steam generator tubing in nuclear power plants [2] and are also widely used in supercritical water oxidation (SCWO) industry [3,4] due to its high strength and excellent corrosion resistance in high temperature. Stainless steel, though always displays higher corrosion rates and weaker corrosion resistance than Ni-based alloy, are also chosen as candidate materials for SCWG in order to reduce the cost.

Extensive studies have been done on the corrosion behavior of Ni-based alloys in a hydrogenated steam environment [5–9] and it could be concluded that the structures of oxides are significantly affected by the content of dissolved hydrogen. Corrosion behavior of Ni-based alloys was also investigated in salt solutions such as Na_2SO_4 [2] and NaCl [10] at subcritical and supercritical temperature, which showed that the corrosive ions can result in pitting corrosion and intergranular corrosion. Moreover, Asselin et al. [4,11–13] used ammoniacal sulfate solution as the corrosion medium to test the corrosion behavior of Ni-based alloys and stainless steels and concluded that sulfate and ammonia, which was not corrosive separately in supercritical water, showed severe corrosion attack to test samples. Cr (III) in the alloy oxide was dissolved and Ni was also preferentially dissolved and formed ammines with ammonia, which both lead the unstable of oxides.

However, little experimental studies are conducted in the environment containing ammonium chloride. The effect of ammonium ion and chloride ion on the corrosion behavior of Ni-based alloys and stainless steel at supercritical temperature are still not totally known.

The present work is aimed to figure out the synergism effect of ammonium and chloride on the oxide structures and corrosion rates of typical Ni-based alloy and stainless steel in supercritical water. The passive films formed on samples were characterized by scanning electron microscope with an energy dispersive spectrometer, X-ray diffraction and laser Raman spectroscopy. Corrosion mechanism would be discussed based on the formation path of oxide films. The purpose of the present work is to obtain quantitative data about constructional materials and to develop anti-corrosion measures for industrial SCWG system.

Experimental section

Materials

The test solution used for the experiment was 6000 ppm NH_4Cl solution which was prepared by deionized water and ammonium chloride (NH_4Cl, >99.5 wt%, Fuchen Chemical Co. Ltd).

Four alloys, Inconel 600, Inconel 625, Incoloy 800 and stainless steel 316 were selected for corrosion testing, which were commercially obtained from A. Finkl & Son company. Chemical compositions of the samples used in the experiment are shown in Table 1. The rod-like raw materials were cut into the cubic pieces of 3 mm × 5 mm × 3 mm by a laser cutting machine. Each of the sample had a hole to be fixed in the reactor. The samples were mechanical polished by SiC paper down to 2500 grit, then they were ultrasonically cleaned by acetone and deionized water. The coupons were stored in a vacuum drying box at room temperature in order to avoid being oxidized in the air.

Table 1 – Composition of metal species in test samples.

Species	Compositions (wt%)			
	Inconel 625	Inconel 600	Incoloy 800	316 SS
Ni	Bal.	Bal.	35	12
Cr	23	17	23	17
Fe	5	10	Bal.	65
Mo	10	–	–	2.5
Mn	0.5	1	1.5	2
C	0.1	0.15	0.1	0.08
P	0.015	0.03	0.03	0.045
Si	0.5	0.5	1.0	1.0
S	0.015	0.015	0.015	0.03

Apparatus and procedures

The test reactor is a batch autoclave which is made of 316 SS. The other parts of the systems, such as coupon holders and valves, are also made of stainless steel. A hot jacket which hanged on the autoclave was used to be the heat resource. A PID controller was utilized to regulate the temperature with a deviation less than 1 °C. In order to eliminate the effect of galvanic corrosion, the samples were fixed by an insulating rod made of diamond, and a sliver wire rather than an iron wire was used to hang the samples in the aim of precluding the interference of Fe ion. Schematic diagram of the sample holder is shown in Fig. 1. Before heating, the whole system was purged by blowing nitrogen gas for 20 min to eliminate the interference of oxygen. Details of the test are shown in Table 2. After each run, the samples were merged into acetone for 30 min and then cleaned by deionized water. The coupons were also stored at a vacuum drying box at room temperature before analyzing.

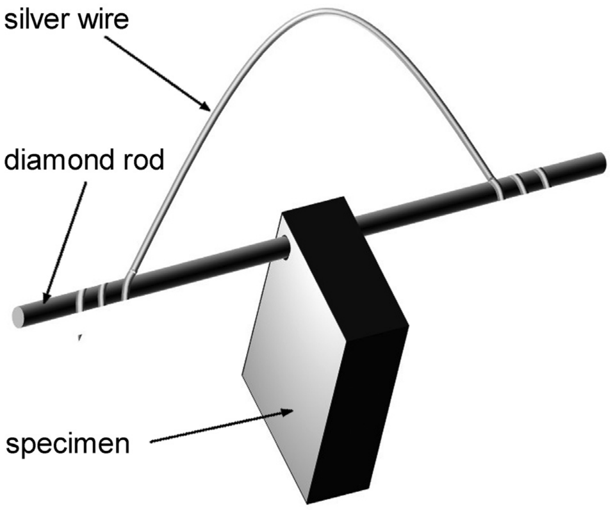

Fig. 1 – Schematic diagram of the sample holder.

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