

Corrosion Behavior of Austenitic Steel 304 in Nearcritical Aqueous Solutions

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Abstract. In this paper, the corrosion characteristics of Austenitic steel 304 in nearcritical aqueous solutions containing 1000 ppm chlorides, and chemical oxygen demand (COD) of 2000 ppm, was investigated. The samples surface were examined using scanning electron microscopy (SEM) equipped with energy dispersive spectroscopy (EDS) and X-ray diffraction (XRD). The results indicated that the most serious corrosion issues occurred at 360°C among three temperatures: 350°C, 360°C and 400°C. The water density and ion products play key roles in influencing the corrosion resistance of alloys under nearcritical aqueous solutions, while effects of temperatures on the stability of the scales are relatively minor. The corrosion resistance of 304 Steel in alkaline solutions was better than that in other solutions. Generally, ~7.5 - 9 was an appropriate pH range.

Introduction

By capitalizing on the properties of water in the supercritical region (above 374.15 °C and 22.1 MPa for pure water), supercritical water technologies, such as supercritical water oxidation (SCWO) and supercritical water gasification (SCWG), have been proven to be an efficient and clean technology to achieve harmless and resource recovery of various organic wastes, respectively. The completely mutually soluble between organic compounds and supercritical water with/without oxidants, so spontaneous and rapid conversion of almost any pollutant occur to oxidize radically pollutants or recover hydrogen rich gases.

Supercritical water processes are high temperature and pressure reactions, to which the feeds preheated up to supercritical conditions generally are necessary. Corrosion of construction materials of pipes & facilities for industrialization implementation of supercritical water technologies is main issues[1]. They take place when the organic compounds treated contain heteroatoms, which can degrade to produce inorganic acids, or the feeds itself bring inorganic anions, such as chloride and bromide etc. Acids and halogen ions are aggressive to process system, especially in the nearcritical water region, normally in the heating and cooling area, where there are higher temperatures and enough larger water density to induce occurrence of electrochemical corrosion. Austenitic stainless steels have exhibited excellent corrosion resistance under traditional industrial applications. Thus, it is of great significance to understand the corrosion behavior of representative stainless steel 304 (S304) in nearcritical aqueous solutions containing chlorides. In this paper, effects of temperatures and pH value on corrosion characteristics of stainless steel 304 are discussed and analysed.

Experimental Section

The aqueous solution with initial pH value of 8.5 used for the corrosion experiments contained 1000 ppm chloride, and chemical oxygen demand (COD) of 2000 ppm for the presence of organic compounds in real wastewater. The main chemical compositions of 304 steel samples are shown in Table 1. Samples of S304 were cut in the form of specimens (15×10×5 mm). The obtained specimens were drilled to have a 3 mm hole near one edge, and then polished progressively with silicon-carbide up to 1600 grit. After cleaning and drying, these specimens were stored for the use of follow-up tests.

In order to avoid the occurrence of galvanic corrosion effects, a delicate corrosion specimen holder was used, detailed information gettable in references [2, 3].

The experimental system adopted in this work was composed of a high temperature autoclave, a temperature controller, a manual metering pump and other auxiliary facilities. Most parts of the used system were made of 316 stainless steel, but the autoclave material was Hastelloy C-276. The autoclave was designed to a maximum pressure and temperature of 35 MPa and 650 °C respectively, with an electrical heating power of 3.0 kW. Other detailed information and operational procedure can be obtained in our previous studies.

Table 1 Chemical Composition of Stainless steel 304

Alloy	C	Cr	Ni	Fe	Mn	Si	Others
S304	≤0.08	19.05	8.95	Bal.	≤2.0	≤1.0	S:≤0.03, P:≤0.035

The microscopic morphology of corrosion products formed specimens surface was observed by a JSM-6390 type SEM, which is equipped with an Energy Dispersive Spectrometer (EDS.) to analyze the chemical composition. This SEM owns a magnification times of 5 - 300000. X-ray diffraction (XRD) analysis using an X'PertProMPD Diffractometer was carried out to determine the phases in the samples after exposure tests. The scanning range was controlled within $2\theta = 10\text{--}100^\circ$ with a step size of 0.001° deg. Cu K_α radiation generated at 60 kV and 55 mA was used for diffraction.

Results and Discussion

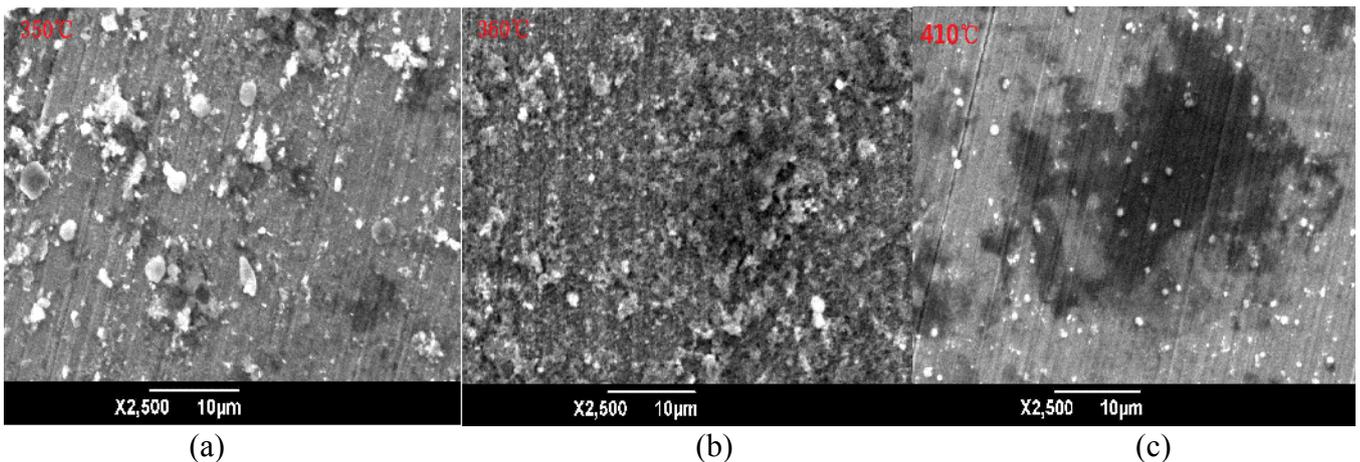


Fig.1 SEM images of the surface morphology of S304 specimens with an exposure times of 60h at three temperature conditions in the solution with initial pH=6.0

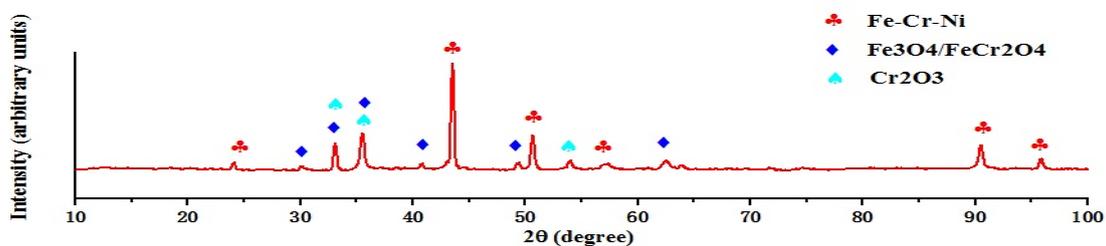


Fig2. XRD patterns of the scales formed on the S304 exposed to nearcritical aqueous solutions at 350°C for 60 h.

The plan-view micrographic images of corrosion products on the S304 specimens after 60 h exposed to aqueous solutions of initial pH=6 containing 1000 ppm chloride under 25 MPa at 350°C, 360°C and 400°C are shown for illustration in Fig.1. For two conditions of 350°C and 410°C, the tested specimens was covered by thinner, protective scales, while a small amount of corrosion product particles occurred on outmost surface. It was great surprising that the corrosion resistance of S304 at 410°C was better than that at 350°C. The scales were primary consisted of chromium-rich

oxides and spinels, as seen in Fig.2[4]. The corrosion resistance of the S304 decreased when testing temperatures increased from 350 °C to 360 °C. After a 60 h - exposure at 360 °C, the ulcerous morphology of S304 specimens emerged. It worth mentioned that comparing with other conditions, the surface loss of alloying elements, especially iron and nickel by chemical dissolution, were catastrophic at 360 °C depending on the surface elements analysis (Fig.3), which could be attributed to the significant increase of ion products of water[5]. The H⁺ concentration increased with the ion products. The increasing solution acidity intensified the dissolution of corrosion products, of which the protective to aggressive species lost. In addition, the stability of protective scales also weakened with an increase in temperatures. Although the higher lability of scales at 410 °C relative to that at 350 °C, the former owned a lower water density and ion products, which resulted in an increase of corrosion resistance.

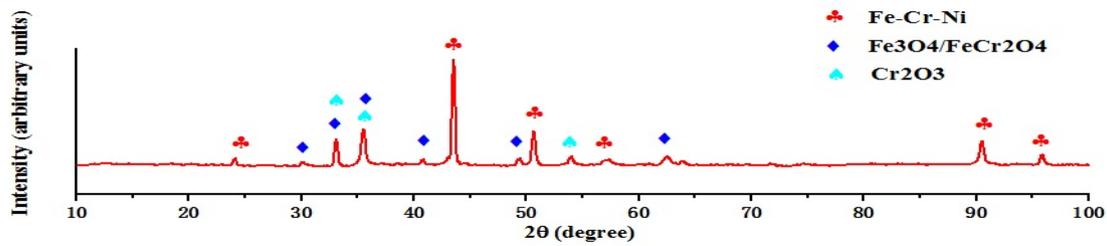


Fig3. XRD patterns of the scales formed on the S304 exposed to nearcritical aqueous solutions at 350°C for 60 h.

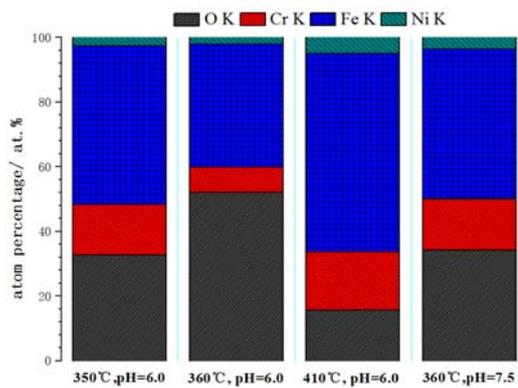


Fig.4 Surface elements distribution of corroded S304 at four conditions

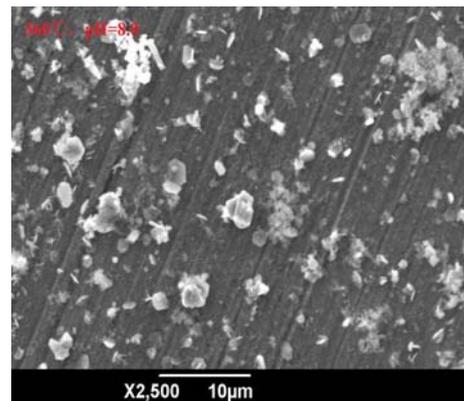


Fig.5 SEM images of S304 specimens after 60 h at T=360°C and initial pH=8.0

Fig.4 indicated the secondary electron images of S304 Specimens after similar exposure conditions to Fig.2 (b) except for a pH value adjusted upward to 8.0. It can be seen that the increasing initial solution pH improved the corrosion resistance of S304, showing the decreased metals loss and enhanced compactness of scales. As mentioned above, aqueous solutions owned a higher ion products at 360°C, suggesting the presence of a high H⁺ content. The H⁺ can facilitate the dissolution of oxides and salts, so the protective effects of corrosion products mainly consisted of oxides against aggressive species receded. If the H⁺ content of initial solutions was neutralize to a lower value, the H⁺ concentration was not excessively high even though the aqueous solutions, under high pressures to refrain from vaporization, were heated to high temperatures, such as 360°C. Thus, the S304H exhibited better corrosion resistance. However, is not the higher the initial pH value, the better corrosion resistance of alloys were. Generally, an appropriate pH range was ~7.5 – 9[6, 7].

Conclusions

1) Under nearcritical aqueous solutions with an exposure pressure of 25 MPa and pH values of 6.0, the most serious corrosion issues occurred at 360°C among three temperatures: 350°C, 360°C

and 400°C. These can be attributed the higher density and ion products of solutions at 360°C. The water density and ion products play key roles in influencing the corrosion resistance of alloys under nearcritical aqueous solutions, while effects of temperature on the stability of the scales are relatively minor.

2) For nearcritical aqueous solutions, initial alkaline solutions can improve the corrosion resistance of alloys. Generally, an appropriate pH range was $\sim 7.5 - 9$.

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