

The role of dissolved oxygen in supercritical water in the oxidation of ferritic–martensitic steel



Zhongliang Zhu, Hong Xu, Dongfang Jiang, Guoqiang Yue, Baorang Li, Naiqiang Zhang*

Key Laboratory of Condition Monitoring and Control for Power Plant Equipment of Ministry of Education, North China Electric Power University, Beijing 102206, PR China

ARTICLE INFO

Article history:

Received 8 July 2015

Received in revised form 26 October 2015

Accepted 26 October 2015

Available online 30 October 2015

Keywords:

Steel

Oxidation

Supercritical water

SIMS

ABSTRACT

To assess the role of dissolved oxygen in supercritical water on the growth processes of oxide scales, a marker experiment of ferritic–martensitic steel was performed by exposing to supercritical water (H_2^{16}O) containing marked $^{18}\text{O}_2$ at 600°C under 25 MPa. The oxide scale was analysed by using Secondary Ion Mass Spectrometry (SIMS). The oxygen isotope profile shows that dissolved oxygen and supercritical water react with metals simultaneously. Dissolved oxygen changes the oxidation/reduction potential of supercritical water leading to an increase in the oxidation rate. The oxidation rate increases with increase in dissolved oxygen content in supercritical water. The mechanism of the effect of dissolved oxygen on oxidation is discussed.

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1. Introduction

The oxidation behaviour of ferritic–martensitic (F–M) steel in supercritical water (SCW) has been widely studied in recent years for applications in the energy industry due to relative good creep resistance, low irradiation activation, good processing ability and modest corrosion resistance [1]. Oxygenated treatment is considered to be an effective chemical water treatment method and is widely used in ultra-supercritical power plants. The boiler components made up of F–M steels are placed in SCW containing dissolved oxygen (DO). A great deal of research on the corrosion of F–M steel in SCW with different contents of DO has been conducted [2–8]. Zhang [2] reported that the weight gains of the F–M steel P92 increase with DO for concentrations from 100 to 2000 parts-per-billion (ppb) in weight at 550°C under 25 MPa. The weight gain from F–M steel T91 tests at 500°C with 25 ppb and 2000 ppb of DO reveal that the oxidation rate is higher in an elevated oxygen concentration environment [8]. The weight gain also increases with the increase of DO concentration during the oxidation of HT9 in the same environment [6]. From these results it may be concluded that under the experimental conditions of SCW with different DO contents, the oxidation rate increases with the increase in DO contents.

Isotope profiles are known to be a powerful tool for determining the direction of mass transport during the oxidation of metals and for understanding oxide growth mechanisms. There have been some experimental procedures concerning the use of stable $^{18}\text{O}_2$ or H_2^{18}O tracers [9–12]. To gain more insight into the roles of oxygen and water vapour species on the growth processes of oxide scales at low pressure, Ehlers [13] investigated the oxidation behaviour of P91 in a $\text{N}_2 + 1 \text{ vol}\% \text{ }^{16}\text{O}_2 + 2 \text{ vol}\% \text{ H}_2^{18}\text{O}$ mixture at a low pressure. Until now, few studies have investigated the role of presence of a small amount of oxygen in SCW on the growth mechanism of the oxide scales of F–M steels.

In this paper, an oxygen isotope tracer experiment of F–M steel P92 was performed at 600°C under 25 MPa in SCW (H_2^{16}O) with a DO ($^{18}\text{O}_2$) content of 2000 ppb, up to an exposure time of 100 h. The aim of this paper is to clarify the role of DO in SCW in the oxidation of F–M steel.

2. Experimental methods

2.1. Materials

The chemical composition of F–M steel P92 is shown in Table 1. Bulk P92 steel was cut into samples of $25 \text{ mm} \times 10 \text{ mm} \times 2 \text{ mm}$. Then, the samples were polished to $1 \mu\text{m}$ surfaces, followed by ultrasonic cleaning in acetone and deionized water. The samples were placed in an autoclave using platinum wires and ceramic insulators to avoid galvanic effects.

* Corresponding author. Tel.: +86 10 61773877; fax: +86 10 61773877.
E-mail address: zhnq@ncepu.edu.cn (N. Zhang).

Table 1
Chemical composition of the F–M steel P92 (mass%).

C	Si	Mn	S	P	Cr	Mo	W
0.10	0.38	0.42	0.001	0.014	8.63	0.37	1.59
V	Nb	Ni	Ti	N	Al	B	Fe
0.164	0.053	0.15	–	0.0385	0.02	0.0013	Bal.

2.2. Apparatus and analysis

The oxidation test using ^{18}O (purity >95%) labelled O_2 as a tracer was performed in a static autoclave. Fig. 1 shows the schematic diagram of the SCW testing facility. The ultrapure water with an electrical conductivity of less-than $0.1 \mu\text{S}/\text{cm}$ was obtained by an ion-exchanger. The water was heated to 100°C and deaerated by bubbling pure nitrogen gas for 10 min. The DO content was measured by METTLER TOLEDO oxygen analyser. The DO content was controlled at 2000 ppb by injecting a mixed gas of argon and $^{18}\text{O}_2$. The autoclave was purged by blowing N_2 for 5 min and then it was vacuum pumped after the samples were placed. The water containing 2000 ppb DO was pumped into the autoclave. The ^{18}O and ^{16}O distribution profiles and the plots of the $^{16}\text{O}/^{18}\text{O}$ ratio through the oxide scale were detected by SIMS, which was used to probe the effect mechanism of DO on the oxidation of F–M steel P92 in SCW. SIMS is a surface analytical technique that focuses a pulsed beam of primary ions onto a sample surface, producing secondary ions in a sputtering process. Analyzing these secondary ions provides information about the molecular and elemental species presented on sample surface. Scanning electron microscopy (SEM) equipped with energy dispersive X-ray spectroscopy (EDS) was used to analyse the morphologies and chemical compositions of the oxide scale. The oxide phases were identified by using X-ray diffraction (XRD). The sample was weighed using a METTLER TOLEDO milligram balance with a sensitivity of 0.1 mg.

3. Results and discussion

Several authors have proposed oxidation mechanisms of F–M steel in SCW [4,7,8,14,15]. The outer layer grows at the oxide/SCW interface due to the outward transportation of Fe ions, and Cr-rich spinel oxide grows at the oxide/metal interface due to the inward transportation of oxidants, which was convincingly demonstrated by a marker experiment [4]. The outward Fe ions migration is the rate-limiting step. Based on the above mentioned oxidation mechanisms, several likely assumptions have been claimed for the plots of $^{16}\text{O}/^{18}\text{O}$ ratio versus oxide depth, which can then be related to the transport and reaction process of $^{18}\text{O}_2$. (1) O_2 only reacts with metal at the oxide/SCW interface. (2) O_2 penetrates down to the metal/oxide interface and O_2 is only involved in a chemical reaction with metal at the metal/oxide interface. (3) O_2 penetrates down to the metal/oxide interface, and O_2 is simultaneously involved in a chemical reaction with metal at the oxide/SCW and metal/oxide interface.

Fig. 2 shows the cross-sectional morphology and corresponding elemental depth profile of the sample exposed to SCW with 2000 ppb DO at 600°C under 25 MPa for 100 h. The phase structure of the sample was confirmed by the XRD spectrum, as shown in Fig. 3. The combination of XRD and SEM/EDS analysis suggest that the outer scale, which has an approximate thickness of $16 \mu\text{m}$, is mainly composed of Fe_3O_4 and the inner layer, which has an approximate thickness of $14 \mu\text{m}$, is Fe–Cr spinel oxide. The internal oxidation zone is also observed between the inner oxide layer and the metal matrix interface.

Fig. 4 shows that the depth profiles of oxygen in the oxide scale after exposure to 600°C SCW containing 2000 ppb $^{18}\text{O}_2$. The concentrations of ^{18}O and ^{16}O were calculated from the measured ion intensities using SIMS. Moreover, the ratio of ^{16}O and to ^{18}O versus depth in the oxide can be obtained and is related to the reaction mechanism and transportation of oxidants (O_2 & H_2O). The curves of ^{18}O and ^{16}O fluctuate slightly in the outer and inner layer, and the changes are slightly intense in the transition layer. Both ^{18}O and

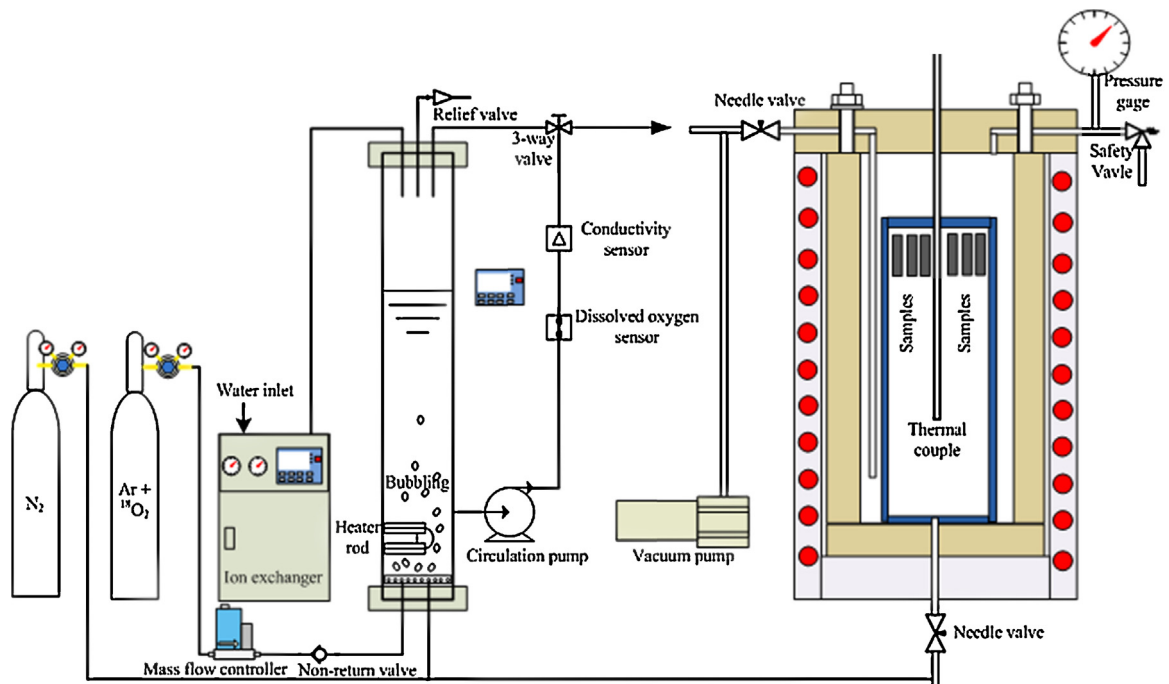


Fig. 1. Schematic diagram of the supercritical water testing facility.

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