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Investigation into the failure mechanism of chromia scale thermally grown on an austenitic stainless steel in pure steam

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ABSTRACT

The corrosion behavior of a commercial austenitic stainless steel HR3C was investigated in air and in pure steam at 700 °C, and the results are compared. The results show that the chromium concentration in HR3C was sufficient to form protective chromia scale initially in both environments. The oxide scales thermally grown in pure steam, however, were apt to lose their protectiveness by cracking and buckling. A failure mechanism of chromia scale thermally grown in pure steam is proposed by considering influences of hydrogen produced during steam oxidation in terms of molecular hydrogen and hydrogen defects.

1. Introduction

The corrosion resistance of stainless steels is usually attributed to the formation of protective chromia scales. In thermal steam environments such as boiler pipes in fossil-fired power plants and oil pipes in steam-injected oil wells, materials are required to form thin protective and adhesive scales for service safety. The thickening oxides in boiler materials would lead to overheating and premature creep rupture by reducing the thermal conductivity, and exfoliation of these oxides can produce blockage of tubes and erosion damage of valves and turbines [1]. It is necessary, therefore, to study the oxidation mechanism of heat-resistant steels in steam.

In past decades, conventional low-Cr ferritic steels (typically up to 2.25%Cr) and 9–12Cr steels (strictly, ferritic-martensitic steels) [2–7] have been studied extensively, and field experiences indicate that use of these steels is limited to steam temperatures up to 620 °C [8]. Austenitic stainless steels with relatively high Cr and Ni, on the other hand, can be used in higher temperatures due to their combination of relatively good creep strength and high temperature oxidation resistance [9]. Extensive studies [10–19] in recent years on the oxidation of austenitic stainless steels (e.g. 304, 310) in wet gases have reported the breakaway oxidation. It seems that the presence of water vapor changes the initial protective Cr-rich oxide scale into a non-protective multilayer scale with a layer of Fe oxides. It is usually considered that the breakaway of protective Cr-rich scale is attributed to the chromium evaporation in the form of $CrO_2(OH)_2$ [11,20–25]. However, the chromium evaporation in low-level-oxygen environments (e.g. pure steam) should be negligible because the formation of volatile $CrO_2(OH)_2$ needs oxygen. According to this perspective, chromium evaporation would not be responsible for the breakaway oxidation of Super 304H in pure steam as found in our previous work [26] where mechanical failure (i.e. cracking) of the initially-formed chromia scale was observed. This remains open to debate.

With above considerations in mind, the present work was performed to investigate the protectiveness of thermally formed chromia scale on a commercial austenitic stainless steel HR3C in pure steam, and to determine its failure mechanism. Based on the characterization of microstructure, chemical compositions and oxide phases, the mechanism for the breakaway oxidation in pure steam was discussed.

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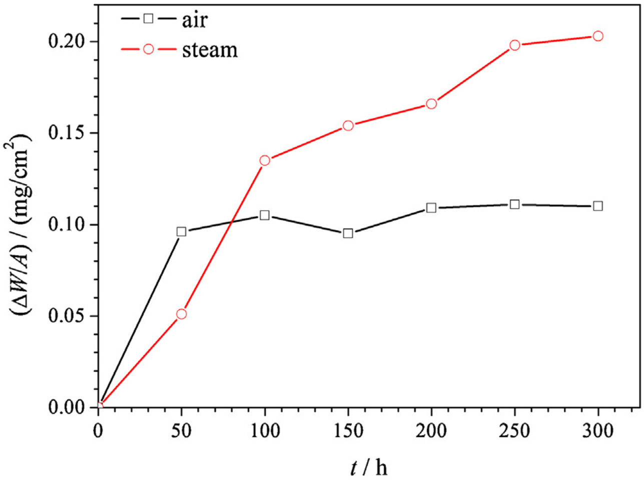

Fig. 1. Mass-gain curves of HR3C steel exposed in two environments at 700 °C.

2. Experimental

Commercial austenitic stainless steel HR3C was studied in the present work and its compositions are listed in Table 1. HR3C tubes as received were cut into coupons with dimensions of 10 × 12 × 2.5 mm^3. All coupons were ground to 1000# with SiC papers and cleaned ultrasonically in distilled water and subsequently in ethanol for 15 min.

Table 1
Nominal chemical compositions of austenitic stainless steel HR3C (wt.%).

Element	Fe	C	Mn	Si	Ni	Cr	Nb	N
wt.%	Bal.	0.06	1.20	0.40	20.0	25.0	0.45	0.20

Isothermal corrosion experiments in pure steam under atmospheric pressure were performed in an apparatus as described elsewhere [26]. Flowing steam was generated by pumping ultra-purified water (resistivity ≥ 10 MΩ cm) containing 8 ppm by weight dissolved oxygen into a pre-heating furnace. Prior to corrosion, the reaction quartz was purged with high-purity argon to prevent the corrosion of samples during the heating process. The test temperature was set at 700 °C and the flow rate of inlet water was maintained at 3 ml/min. Samples were furnace cooled after the tests to room temperature in high-purity argon. The linear velocity of steam flow roughly calculated from the ideal gas equation was 14.13 cm/s. For comparison, isothermal corrosion tests in air were conducted in a muffle furnace at 700 °C.

The corroded specimens were characterized carefully in terms of scale microstructure, phase identification and chemical composition. Scale microstructures were investigated by a Scanning Electron Microscopy (SEM). For metallographic cross-section preparation, the corroded specimens were Ni-coated prior to mounting to protect the oxide scales during grinding/polishing and to reveal a clearer contrast between oxide scale and mounting material. Oxide phases were identified by Grazing Incidence X-ray Diffraction (GIXRD) with an incidence angle of 0.5 °. The chemical compositions of the oxide films by XPS were finished with an ESCALAB250 using Al Kα radiation ($h\nu$ = 1486.6 eV) at a pass energy

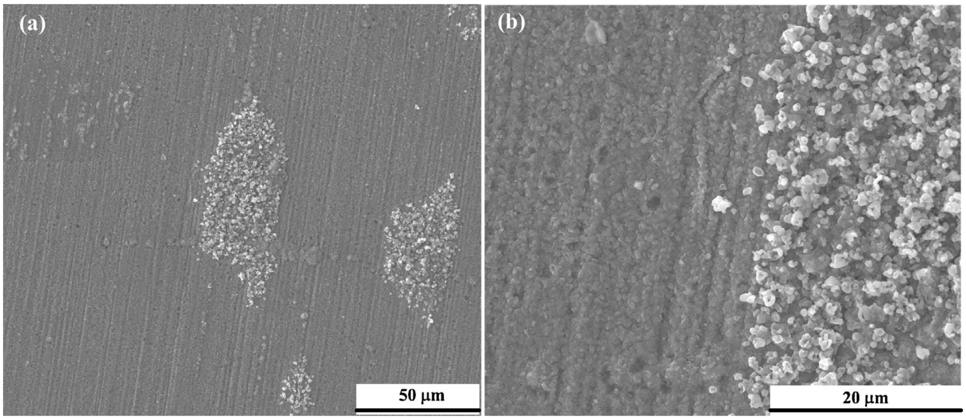

Fig. 2. Surface morphologies under (a) low magnification and (b) high magnification of HR3C steel after 300 h exposure in air.

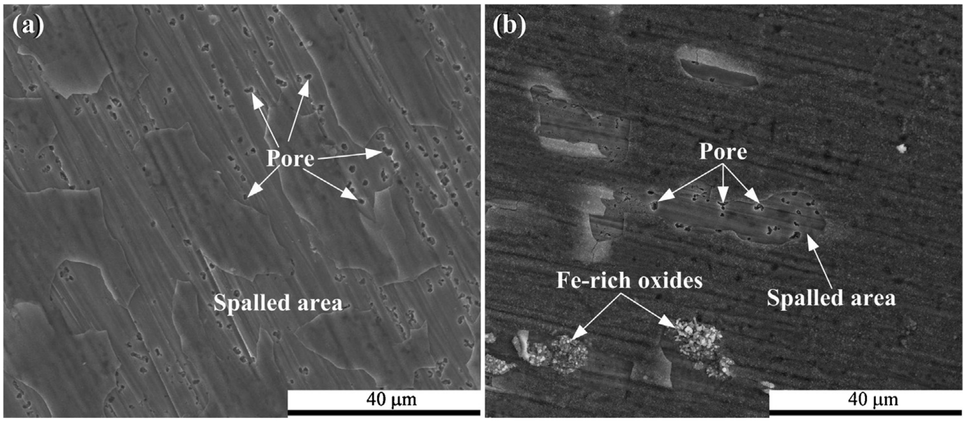

Fig. 3. Surface morphologies of HR3C steel after (a) 50 h and (b) 200 h exposure in steam.