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Study of the scale formed on super 304H boiler tube steels after long-term steam oxidation at high temperatures

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ABSTRACT

Steam oxidation of a Super 304H boiler tube was performed at steam temperatures of 650 °C and 700 °C for time durations up to 5000 h. The oxidation scale outcomes which formed on as-received untreated and shot-peened (SP) tubes were studied using X-ray diffraction (XRD), scanning electron microscopy (SEM), electron backscatter diffraction (EBSD), and transmission electron microscopy (TEM). γ-Grain nanocrystallization on the surface of the SP specimen generated an abundant fraction of grain boundary that guaranteed the formation of a continuous amorphous SiO_2 layer at the metal-scale interface that enhanced the formation of dense Cr_2O_3 and $FeCr_2O_4$ in the scale. Scale breakaway along defects in the outer layer of the scale was accelerated by the steam temperature in the untreated specimens, whereas the scale that formed on the SP specimens appeared to be stable.

1. Introduction

The conventional coil-fired thermal power plant is still the most important electric energy source, though much of the effort in research and related projects has focused on renewable energy technologies [1]. Increasing the steam temperature from 600 °C to 700 °C in relation to ultra-supercritical (USC) and advanced USC (A-USC) technologies increases the thermal efficiency while also reducing of CO_2 emissions [1,2]. The development of materials for use in critical environments must consider the combined properties of the creep strength and oxidation resistance. The current types of steel used in the construction of boilers with steam temperatures above 600 °C have replaced of traditional martensitic 9–12%Cr steels and are mainly high alloyed austenitic stainless steels [1,3,4]. Over the past three decades, a database of the creep and oxidation properties of the ferritic-martensitic (F-M) materials [5–9], particularly 9%Cr heat resistant steels, has become well established [4,7,10–14]. The development and characterization of austenitic stainless steels are critical for valuable guidance and to build a database to ensure the safety of A-USC boilers.

In a power plant, corrosion scale formed on boiler tubes is an even more serious problem than creep damage because it can break away and flow with high-pressure steam and can destroy the steam turbine systems. Understanding the scale formation mechanism and enhancing the corrosion resistance methods which can be used with F-M steels have been topics of much study [7–14]. Authors agree that the formation of dense layers enriched in Cr ($FeCr_2O_4$) that separate the metal from the corrosion environment is the main issue related to corrosion resistance. For example, general considerations include increasing alloy concentrations from martensitic to austenitic in boiler tubes [3] and surface treatments by shot-peening (SP) [15–20], as well as a recently reported novel method of pre-oxidation [4].

The characterization of oxide phases has become important in relation to the design and control of oxidation-resistant layers. A microstructural analysis of the oxide features includes a compositional analysis using EDS and a structural analysis using XRD, EBSD and TEM. For F-M steels, traditional EBSD has been a powerful means of a visible analysis of the oxide phase distribution in scale because Fe-enriched oxide (Fe_2O_3, Fe_3O_4) and Cr-enriched oxide ($FeCr_2O_4$) have different crystal structures with an α matrix [8,11]. However, these processes are challenging when conducted with austenitic stainless steels because Fe_3O_4 and $FeCr_2O_4$ have the same crystal structure with a γ matrix [21].

Super304H (S304H) steels are candidate material for the A-USC plants. At presents, they are partially used in modern USC plants and have been field-tested in A-USC power plants. The database on the creep property of the S304h boiler tube has been established [1,3], however, the long-term oxidation behavior is rarely reported. Authors and steel makers agreed that the efficiently enhancement of oxidation resistance by shot-peening treatment, however, the reason is still under

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debate. Understanding the oxidation mechanisms may give useful guidance for the steel makers to make even better product, and that is particularly meaningful for the domestic maker. Indeed, we are field-testing the boiler components which are fabricated by the S304H tube (and with other types of tubes). It is believed that the combined use of the field-tested and laboratory-tested data will be powerful for the later assessment of the tested tubes. Therefore, the objectives of this study were to establish a database of the long-term steam oxidation behavior of S304H boiler tubes, focusing on the study of the oxide phase features and shot-peening effects. High-temperature steam tests were performed on as-received untreated and steam-side peened boiler tubes in a laboratory. The oxide phases and their distributions within the scale were systematically studied by the modern combined analysis techniques.

2. Experimental Procedures

2.1. Materials and Steam Test

Boiler tubes of S304H [3] and of steam-side shot-peened steels were purchased from NSSMC with the following specifications: an outer diameter of 50.8 mm and a wall thickness of 4.0 mm. These are identified as untreated and SP, respectively, henceforth. The chemical composition was measured by optical emission spectrometry (OES) (mode ARL-3460), as listed in Table 1, with the element concentrations in the ranges of their respective specifications. Several tubes in the as-received condition with a length of 10 mm were cut and used in the long-term steam test. Fig. 1 shows a schematic diagram of the setup of the long-term steam test facility. First, distilled water was sent to a quartz tube coil and heated by a furnace to generate critical steam. Then, the critical steam was further heated to the target temperature (500–900 °C) by subsequent furnaces. Samples were loaded onto a quartz holder located in the center of the heating furnace. Finally, the steam was cooled to water. Several K-type thermocouples and flow sensors were used to control and monitor the temperature of the steam environment. The prepared tubes were tested with steam temperatures of 650 °C and 700 °C and with time periods of 1000 h, 2000 h and 5000 h. After the oxidation test, a thick crystal bond was coated onto the surface of the coupons to prevent the scale from dropping off during the cutting step, and this was dissolved by acetone to prepare the samples for the final microstructural investigation.

2.2. Microstructural Analysis

The microstructural investigation of the samples included surface XRD and SEM analyses, cross-sectional SEM, EBSD, and TEM. The XRD measurement was carried out on a Rigaku SmartLab 9 kW system with Cu-kα_1 radiation operated at a tube voltage and current of 45 kV and 200 mA, respectively. The step size was set to 0.02°. A high-speed one-dimensional X-ray detector was used to speed up the measurement at 10° per min. The XRD data analysis was performed using PDXL2 software with the ICDD2016 database. Cross-sectional SEM samples were prepared by metallographic polishing and were observed by means of JSM-5610 and JSM-7001F SEM analyses. Specimens for EBSD mapping were prepared by metallographic polishing and finished by fine polishing in a colloidal silica solution for 2 h. EBSD measurements of the as-SP samples were carried out on a TSL-OIM system mounted on a TESCAN MIRA II FESEM. Measurements of the oxide phase distributions in the scale were conducted on an Oxford Aztec HKL system mounted on a Zeiss Merlin FESEM. Combined EBSD and EDS was used to map the phase distributions in the scale. Cross-sectional samples for the TEM analysis were prepared by a focused ion beam (FIB) on a Zeiss Auriga dual-beam system. TEM observations were conducted using a JEM ARM 200F system operated at an accelerated voltage of 200 kV. The predication of the oxide phases in the scale was conducted with Thermo-Cal software with the TCFE7 database.

3. Results

3.1. Untreated and SP

Fig. 2 shows the microstructures of the S304H samples before the steam test. Fig. 2a and b are SEM secondary electron (SE) images showing the surface morphologies of the untreated and SP specimens, respectively. A grain-like surface was observed on the untreated sample. The cross-sectional SEM images and the EDS results suggested that it was a layer approximately 1 μm thick with the main composition of the Fe-15Cr-5Ni-4O (in wt%) composite which was s to be formed during the production of the tube [22]. After the SP treatment (Fig. 2b), the surface became smooth with a dimpled morphology. The EDS results showed that the surface chemical composition was very similar to that of the matrix, indicating that the composites formed during production were removed by the subsequent SP treatment.

Fig. 2c shows the microhardness profiles of the untreated and SP specimens, where the depth of surface hardening is up to ~400 μm from the treated surface. The hardness value of the top surface is as high as ~450 HV, which decreases to its original value of ~200 HV gradually with an increase of the depth from the surface. Fig. 2d shows an EBSD image quality (IQ) map of the SP sample, showing a severely deformed microstructure on the treated surface with a deformation depth of ~90 μm from the treated surface. The grain size near the surface up to a depth of 10 μm was fine ($<$ 100 nm) such that it could be observed by EBSD, whereas it increased to its original value (~15 μm) as the depth increased from the top of the treated surface. We used a depth-specific [22] plan-view TEM sampling method to prepare the thin foil samples near the surface region. Fig. 2e and f show TEM dark-field (DF) images with the corresponding selected-area diffraction patterns (SADP) recorded at a depth of ~5 μm from the top of the treated surface of the SP specimen. In Fig. 2d, a large number of bright areas which show $(111)_\gamma$ grains with an average grain size of ~30 nm can easily be observed, suggesting surface nanocrystallization in the SP specimen. The ring pattern shown in the corresponding SADP (Fig. 2e) further indicates that nanograins with random misorientations formed. Indexing of the SADP found that the crystal structure of the nanostructure is the γ-phase, suggesting that there was no phase transformation during the SP treatment. It is known that austenitic stainless steels, for example, SS304, SS316, and SS304H, appear to undergo strain-induced martensitic ($\gamma \rightarrow \alpha'$) transformation during high strain deformation [15,23,24]. The absence of martensite grains upon shot-peening was presumably related to the large amount of NbC dispersed in the matrix, which was not clear and under our investigation. Those observations indicated that the SP not only removed the fabrication oxide but also introduced a nanostructured surface with a thickness of ~10 μm on the S304H steel.

Table 1
OES measured chemical composition (wt%) of the S304H specimens.

Elements.		C	Mn	Si	P	S	Ni	Cr	Nb	Cu	Fe
Specification	Min	0.07	–	–	–	–	7.50	17.0	0.30	2.5	Bal.
	Max	0.13	1.00	0.30	0.04	0.01	10.5	19.0	0.60	3.5	Bal.
Measured		0.07	0.86	0.27	0.03	0.001	8.52	18.50	0.57	3.0	Bal.