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Intergranular corrosion susceptibility of a novel Super304H stainless steel

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ABSTRACT

The newly developed Super304H austenitic stainless steel is being widely used in ultra supercritical fossil fired boilers because of its superior high temperature strength, good oxidation resistance and steam corrosion resistance. But its high carbon content increases greatly its intergranular corrosion susceptibility. A 1000 MW ultra supercritical fossil fired boiler being installed in South China experienced a severe superheater leakage accident recently during a water pressure testing. After failure analysis, it was found that the superheater tubes, made of Super304H, were attacked by stress corrosion cracking which was induced by intergranular corrosion. The external reason for the intergranular corrosion was the bare laying of the tubes at seaside environment for a few months and the internal reason was the very high intergranular corrosion susceptibility of the tubes. This aroused our concern on the intergranular corrosion resistance of this material and further experiment was carried out by selecting different batches of Super304H tubes to evaluate their intergranular corrosion susceptibility. The conclusion was that the high intergranular corrosion susceptibility of the Super304H tubes might be induced by the unqualified match of carbon and niobium or the improper delivery heat treatment technology. It is therefore strongly recommended that more attention be paid to this novel material regarding its intergranular corrosion susceptibility and the chemical composition and delivery state heat treatment technology for standard specification of this material should be further investigated and optimized.

1. Introduction

Ultra supercritical fossil fired boilers have been rapidly developed recently to lower energy consumption, increase productivity and reduce environment pollution. A novel Super304H austenitic stainless steel, being recently developed by Sumitomo Metal Industries of Japan, has been widely applied in ultra supercritical fossil fired boilers to fabricate superheater and reheater tubes because of its superior high temperature strength, good oxidation resistance and steam corrosion resistance [1–5]. But the very high carbon added in Super304H stainless steel to improve its creep property has increased its intergranular corrosion susceptibility especially when it works at high temperature as superheater and reheater tubes. At this moment, the main research concerns are focused on the high temperature creep and oxidation properties of the material but little attention has been paid to its intergranular corrosion susceptibility, which may be quite severe because of its high oversaturated carbon content. Meanwhile, the standard specification for the delivery state heat-treatment of Super304H stainless steel is a two-stage high temperature solution treatment at 1250 °C and 1150 °C respectively, which seems not able to assure the sufficient formation of niobium carbonitrides (Nb(C,N)) to constrain the carbon, thus the danger of chromium carbide ($Cr_{23}C_6$) formation in this material seems not totally avoidable at its working temperature around 650 °C, a very

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sensitive temperature for chromium carbide formation. That is to say, if niobium carbonitrides have not been formed sufficiently in this material to constrain the high oversaturated carbon element because of improper composition design or heat treatment technology, the working temperature and the high carbon content in the material would easily result in the mass formation of chromium carbides, thus bring about strong intergranular corrosion tendency of the material.

A 1000 MW ultra supercritical fossil fired boiler being installed recently in South China experienced a severe superheater leakage accident during a water pressure testing and the superheater tubes were made of Super304H stainless steel. Similar failure case was also reported in other power plant in China [6]. This aroused our great concern on the practical intergranular corrosion resistance of this novel Super304H stainless steel which is being greatly promoted to apply in ultra supercritical fossil fired boilers all over China. In this paper, concerning the superheater leakage accident happened in the power plant in South China, failure analysis was first made to find the reason for the leakage of the superheater tubes. Secondly, the intergranular corrosion susceptibility of some as-received Super304H tubes was evaluated by Method E in GB/T4334-2008 (ISO3651-1998). Finally, we brought forward our concern and suspicion on the intergranular corrosion resistance of this novel Super304H in practical application as superheater and reheater tubes in ultra supercritical fossil fired boilers.

2. Experiments

One leaked and four as-received Super304H austenitic stainless steel tubes with specification of $\Phi 48.5 \times 6.5$ mm were employed as the experimental material. Chemical composition was measured by Vacuum Spark Emission Spectrometer (Foundry-Master, WAS, Germany) and nitrogen element was especially measured by Photoelectric Emission Spectrometer. Optical micrographic observation was made on Zeiss microscope. Energy Diffraction Spectra (EDS) analysis was carried out on LEO1530VP Scanning Electron Microscopy (SEM).

Intergranular corrosion susceptibility was evaluated by Method E in GB/T4334-2008 (ISO3651-1998)-Corrosion of Metals and Alloys—Test Methods of Intergranular Corrosion of Stainless Steels. Method E: Bend specimens are immersed in the soft boiling solution of sulfuric acid (H_2SO_4) + copper sulfate ($CuSO_4$) + copper chipping for 16 h before bending test. Bend specimen preparation: for each tube, five longitudinal bend specimens were machined with a size of $80 \times 10 \times 5$ mm (length/width/thickness). One specimen was bended only without any other treatment, which was used as a comparison base. Two specimens were immersed in the above solution for 16 h and then bended. The last two specimens first went through sensitivity heat-treatment at 650 °C for 2 h and then were immersed in the solution for 16 h before bending test. Bend test was made on REGER RGL-20A Universal Testing Machine.

3. Results

3.1. Macrographic observation of the leaked tube

Nondestructive penetration test on the leaked tube demonstrated one visible crack near the weld, as shown in Fig. 1a. After the crack zone was ground and polished, more macro cracks were visible, as shown in Fig. 1b. It can be seen from Fig. 1. that the cracks are parallel to the weld with 6–7 mm away from and no obvious plastic deformation is found around the cracks.

3.2. Chemical composition

Chemical composition of the leaked Super304H superheater tube was measured and shown in Table 1. From Table 1, we know that the composition of the leaked Super304H tube is fully up to the grade of ASME standard and Chinese GB standard.

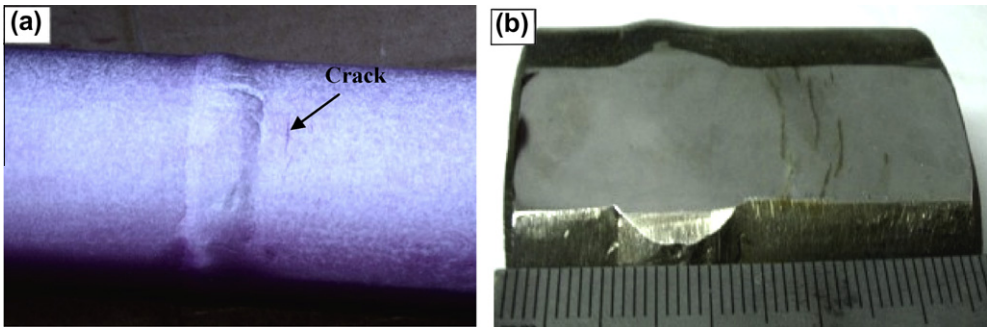

Fig. 1. Macrograph of the leaked tube (a) the crack after penetration, (b) the cracks after polishing.