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Effect of grain size on self -healing behaviour of sensitized S304HCu stainless steel

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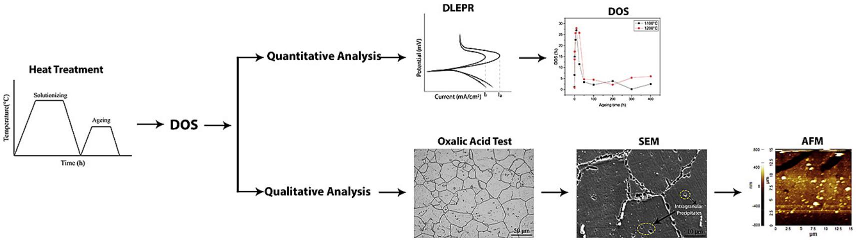
HIGHLIGHTS

- Coarse grains accelerate sensitization and retard the healing rate.
- Diffusion mechanisms favouring sensitization and healing are identified.
- Oxalic acid test is unable to detect desensitisation.
- DLEPR test is superior to oxalic acid test to evaluate DOS and healing.

GRAPHICAL ABSTRACT



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ABSTRACT

S304HCu stainless steel is extensively used for superheater and reheater applications in power plants due to its superior creep strength and oxidation resistance which are derived from the coherently dispersed precipitates formed in austenite matrix. In addition to the beneficial precipitates, chromium carbide precipitates can also form. Formation of chromium carbide precipitates during service will lead to sensitization. In this investigation, S304HCu samples were solutionized at 1100 °C and 1200 °C for 1 h, and further aged at 750 °C for upto 400 h to introduce sensitization and subsequent healing. The influence of ageing time and grain size on the degree of sensitization (DOS) was evaluated by using oxalic acid and double loop electrochemical potentiodynamic reactivation (DLEPR) tests. DOS initially increased up to 10 h of ageing and subsequently was reduced due to healing and attained a steady value at 50 h. Faster and higher DOS was observed in coarse grain structure than in the fine grain structure. However, healing was largely delayed in coarse grained structure. The difference in solute and excess vacancy concentration and shifting of the nose in TTP curve were attributed to the difference in the kinetics of sensitization and healing. The extent of the attack on the grain boundary was analyzed using AFM.

1. Introduction

The thermal efficiency of power plants can be increased by operating them at higher temperature and pressure [1,2]. The operating temperature and pressure in advanced ultra supercritical (AUSC) power plants are up to 760 °C and 35 MPa, respectively [2,3], which requires materials with high creep strength and good oxidation resistance. Austenitic stainless steels are traditionally considered for the power plant applications. Among the austenitic stainless steels, copper added austenitic stainless steel S304HCu receives greater attention as a boiler grade material for superheater and reheater tubes due to its high creep strength and oxidation resistance [1,3–6]. S304HCu differs from the conventional 18–8 austenitic stainless steel by the addition of copper (3%), niobium,

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boron and nitrogen and higher carbon content. Copper enhances the creep strength at high temperature by the formation of coherently dispersed fine copper rich precipitates in the austenitic matrix [7]. Nitrogen and niobium combined with carbon form Nb(C, N) precipitate during service temperature and improves the creep strength [3,4]. Further nitrogen and tungsten enhance the strength by solid solution strengthening effect [1]. Boron addition enhances the number density of the chromium carbides along the grain boundaries and suppresses grain boundary sliding and surface cracking tendency which helps in increasing the creep rupture strength [8].

The superheater and reheater operating at high temperatures for a long time can undergo changes in its properties because of microstructural degradation caused by cyclic and continuous thermal exposure. This could lead to premature failure during service of the superheater and reheater components in their lifespan. When austenitic stainless steels exposed to temperatures ranging from 450 to 850 °C, chromium carbide can form at the grain boundaries by depleting chromium from regions next to the grain boundaries [9–12]. This phenomenon is called “sensitization” and it renders the chromium depleted regions susceptible to intergranular corrosion (IGC).

Carbide precipitates are classified into three categories based on their size and morphology: large irregular carbides, intermediate carbides, and intragranular carbides. The large irregular carbides of the size 500–2000 nm formed along the grain boundaries like a discontinuous plate and grow into the grains on both sides of the grain boundary. The intermediate carbides in the size of 100–300 nm also formed along the grain boundaries but it grows into the grain on only one side of the grain. Intragranular carbides formed in the grain interior in a massive amount and the size of the precipitates is 45–90 nm. The size of the precipitates may vary depends upon the growth rate and location, but the chemical composition is same for all the precipitates. Molybdenum can also be present in these carbides if the alloy is subjected to prolonged thermal exposure [13].

Several theories have been proposed to explain the sensitization mechanism. Some of the popular theories are: (i) chromium depletion theory, (ii) segregation theory, and (iii) noble carbide or electrochemical theory [14–17]. Among these three, chromium depletion theory is a widely accepted one. As per this theory, stainless steels are sensitized by the formation of Cr carbide along the grain boundaries and the Cr depleted zones adjacent to grain boundaries. These Cr depleted regions are susceptible to IGC [18,19]. Several methods like Strauss, Huey and Streicher tests are available to detect the susceptibility of an alloy to sensitization and the extent of IGC attack [20–22]. These tests require more volume of materials and fail to evaluate the degree of sensitization at low levels. ASTM 262 practice A can also be used to detect the susceptibility to sensitization [21–24]. But this method is only qualitative and does not quantify the extent of sensitization [22,25]. Whereas, an electrochemical technique viz., electrochemical potentiodynamic reactivation (EPR) method is currently used to quantify the degree of sensitization (DOS). This method was introduced by Cihal et al. in 1969. Based on the potential scanning mode EPR technique is categorized into two methods viz., single loop EPR (SLEPR) and double loop EPR (DLEPR). SLEPR method proposed by Clarke et al. in 1977 [23,26,27] and Akashi et al. developed the DLEPR in 1980 [27]. The merits of this DLEPR test are: quantitative, non-destructive and less time-consuming. It can also be used to evaluate the low level of sensitization and for in-situ in field measurements and site examination [20,23,28].

Self-healing is a phenomenon by which desensitization of the sensitized regions is effected by enriching the chromium concentration through diffusion of chromium from grain interior to grain boundary. As a result of self-healing, the amount of Cr in the Cr depleted region is raised to more than the critical level so that corrosion resistance of that region is regained.

Solutionizing of stainless steels is performed to attain a uniform composition throughout by complete dissolution of precipitates. The extent of dissolution of the precipitates depends on the solutionizing temperature and the temperature at which the concerned precipitate starts dissolving. However, this treatment will also decide the grain size. The higher the solutionizing temperature the larger the grain size. Grain size can influence sensitization and desensitization behaviour. During service, exposure to the operating temperatures will lead to the formation of precipitates in the solution treated stainless steel, resulting in an improvement in strength and creep resistance.

The present work aims to evaluate the degree of sensitization in S304HCu samples solutionized at 1100 °C and 1200 °C for 1 h and subsequently exposed to 750 °C up to 400 h. Though this alloy is used for operating temperature about 650 °C, the experimental ageing was performed at 750 °C in order to accelerate the process of sensitization and desensitization. The DOS of the aged samples was evaluated using oxalic acid etch test and DLEPR test.

2. Material and methods

2.1. Heat treatment and sample preparation

S304HCu stainless steel samples of size 20 × 20 × 5 mm were used for this present study and its chemical composition is listed in Table 1. Two sets of samples were solutionized at two different temperatures i.e., 1100 °C and 1200 °C for 1 h and then water quenched. Subsequently, the solutionized samples were aged at 750 °C for different ageing periods (0.5, 1, 10, 25, 50, 100, 200, 300 and 400 h). The designation assigned for these samples, which will be used in the forthcoming discussion is shown in Table 2.

Samples for the metallographic study were prepared by following conventional polishing technique. The polished samples were etched electrolytically with 10% oxalic acid solution (10 g oxalic acid+ 100 ml distilled water) for 90s as per ASTM A262 practice A. After etching the microstructures were recorded at different magnifications using an optical microscope. Grain size was estimated by linear intercept method as per ASTM E112. The grain size distribution was analyzed using commercial ImageJ software. Scanning electron microscopic study was performed to identify the location of the precipitates in the aged samples.

2.2. DLEPR test

DLEPR test was performed as per ASTM G108 using Gill AC, ACM instrument potentiostat. Prior to the test, the samples were polished with emery papers to get rid of the oxide layers and then cleaned with acetone. The DLEPR test was performed in a solution of 0.5 M H_2SO_4 + 0.01 M KSCN on an exposed area of 1 cm^2 using a standard three-electrode electrochemical cell. KSCN acts as an activator or depassivator to increase the reactivation current. The test sample, a platinum foil and a saturated calomel electrode (SCE) were the working, auxiliary and reference electrodes, respectively. Reference electrode measures the potential of the solution – sample interface and the auxiliary electrode measures the current flow. In the beginning of the test, the samples were immersed in the test solution till the attainment of a steady open circuit potential (OCP). In order to determine the maximum current density in the anodic scan (I_a), the samples were anodically polarized in the voltage range from −500 mV to +700 mV with reference to the OCP at a scan rate of 100 mV/min [15,16]. Then the applied potential was reversed at the same scan rate to initial potential to determine a