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Investigation of the sensitization and intergranular corrosion of tube-to-tubesheet welds of hyper duplex stainless steel using an electrochemical reactivation method

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ABSTRACT

The sensitization and intergranular corrosion associated with a phase transformation of tube-to-tubesheet welds of hyper duplex stainless steel were investigated using modified double loop electrochemical potentiokinetic reactivation. The susceptibility to sensitization of the hyper duplex stainless steel tube-to-tubesheet welded with an Ar shielding gas supplemented with nitrogen gas decreased owing to a decrease of the ferrite phase fraction and precipitation of chromium nitrides, thereby increasing the intergranular corrosion resistance. The intergranular corrosion in the hyper duplex stainless steel welds was selectively initiated at the Cr-depleted regions adjacent to the chromium nitride precipitates in the ferrite phases.

1. Introduction

Duplex stainless steels (DSSs) have been increasingly used for various applications such as desalination facilities, power plants, off-shore petroleum facilities and chemical industries owing to their high resistance of corrosion in the harsh environment. DSSs with an equal fraction of a ferrite (α) phase and an austenite (γ) phase not only have great mechanical properties but are also relatively inexpensive as compared with austenite stainless steels (ASSs) owing to the addition of low amounts of Ni [1–3]. Hyper duplex stainless steels (HDSSs) are defined as highly alloyed DSSs with a pitting resistance equivalent number (PREN = wt.% Cr + 3.3 (wt.% Mo + 0.5 wt.% W) + 16 wt.% N) of 45–50 [2]. The corrosion resistance of DSSs is determined by the proper fractions of α and γ-phases and by the Cr-depleted zone adjacent to secondary phases such as sigma (σ) phase and chi (χ) phase, carbides and, nitrides [4,5].

Regardless of the superior corrosion property of DSSs, their resistance to corrosion may be significantly deteriorated in DSS welds during solidification after welding depending on the welding conditions. In the heat affected zone (HAZ) and the weld metal (WM), the microstructure undergoes rapid heating and cooling cycles, which results in excessive ferritization [6–8]. Furthermore, undesirable phases such as chromium carbides, chromium nitrides, σ-phases, and χ-phases are prone to be formed during the welding process. Especially, when DSSs are welded with low heat input using a pure Ar shielding gas, resulting in a rapid cooling rate, chromium nitride (Cr_2N) is precipitated in the matrix of the α-phase due to low solubility of nitrogen in the α-phase (<0.05 wt.%), whose structure is body-centered cubic [9]. Cr_2N precipitates from the α-phase by nucleation and growth, followed with a kinetic "C" curve. Nucleation occurs at dislocations, inclusions, α/γ interfaces, and the interior of grains as well as at the grain boundaries in the α-phases [10–12]. Cr_2N forms the Cr-depleted zone in the surroundings and causes localized corrosion in the α-phase [13]. Hence, suppression of the γ-phase transformation on cooling and the resultant increase in the α-phase fraction and precipitation of Cr_2N can result in a degradation of the corrosion properties of the WM and HAZ [14]. In order to resolve these issues, the following are important in term of corrosion: control over the post weld heat treatment [15–17], the heat input [18,19] and cooling rate [20], the use of a filler metal, the adding of nitrogen gas in the shield gas [7,21–26], and the post weld cleaning of weld metal [27].

However, it has also been observed that even though expensive filler metals that contain nitrogen are used, weldments of nitrogen

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containing DSSs suffer from pitting attack due to loss of nitrogen during welding. So, mixing of nitrogen gas (N_2) in the Ar shielding gas could be the most effective solution to prevent loss of nitrogen during welding and maintain an optimum γ-phase to α-phase ratio in the weld and increase the pitting corrosion resistance of such weldments [9,23,28,29,3]. The addition of N_2 to the Ar shielding gas has positive effects as follows: nitrogen is the important element for providing phase balance under weld-cooling conditions due to a strong γ-stabilizer [30]. In addition, nitrogen decreases the Cr_{eq}/Ni_{eq} ratio and increases the transformation temperature of the α-phase to γ-phase, thereby increasing the fraction of γ-phase [31]. In addition, the increasing N_2 content in the Ar–N_2 mixture changes the morphology of the welds from an acicular to a globular form of the γ-phase [28]. However, it is difficult to locate studies that have quantitatively elucidated the effects of N_2 addition in the Ar shielding on the sensitization and intergranular corrosion related to the microstructure such as high α-phase fraction and Cr_2N precipitations in the HDSS with high nitrogen (0.34 wt.%), compared to the DSSs with low and medium nitrogen (0.15–0.25 wt.%). So, further in-depth researches of intergranular corrosion behaviour associated with the phase transformation are required.

There are a number of standard methods on the intergranular corrosion, such as oxalic acid test, Huey test, Strauss test, Streicher test and Copper–Copper Sulphate-50% sulphuric acid test, which can be used to evaluate the intergranular corrosion resistance. However, none of these methods are a quantitative and non-destructive method. Moreover, performing the above mentioned tests is time consuming. Hence, much research has been conducted to innovate a test method to estimate the intergranular corrosion resistance by developing the electrochemical potentiokinetic reactivation test (EPR). EPR is a quantitative method which indicates degree of sensitization based on electrochemical parameters obtained from the potentiodynamic polarization curve [32–38]. During the past decades, researchers have quantitatively evaluated the intergranular corrosion resistance associated with the degree of sensitization using the double loop electrochemical potentiokinetic reactivation (DL-EPR) method, which indicates the degree of Cr depletion that occurs adjacent to Cr-rich phases formed in stainless steels such as Cr-carbide, σ-phases, and α′-phases [39–41]. However, since it is difficult to locate studies that have evaluated the intergranular corrosion resistance associated with the degree of sensitization which indicates the degree of Cr depletion adjacent to Cr_2N in HDSS welds using the DL-EPR test, further in-depth study is needed.

Hence, in this work, to elucidate the sensitization and intergranular corrosion of tube-to-tubesheet welds of hyper duplex stainless steel, thermodynamic calculations of the phase diagram and equilibrium fractions of each phase, optical microscopy (OM), X-ray diffraction (XRD), scanning electron microscopy (SEM) attaching the energy dispersive spectroscopy (EDS), and transmission electron microscopy (TEM) attaching the EDS and a DL-EPR test were carried out.

2. Experimental procedures

2.1. Materials and heat-treatment

After HDSS plates with a thickness of 4 mm were cold rolled and annealed at 1090 °C, producing sheets with a thickness of 1.5 mm. HDSS tubes with an outer diameter of 19.05 mm and a thickness of 1.5 mm were manufactured using the gas tungsten arc welding method with a heat input of 0.08 kJ/mm. The tubes were solution heat-treated at 1090 °C for 3 min per 1 mm thickness followed by quenching in water. In order to prepare the HDSS tube-to-tubesheet welds, HDSS plates with a thickness of 8 mm were hot rolled and solution annealed at 1090 °C. Holes were then drilled in the plates. To obtain the comparative conditions of the shielding gas, the tubes were inserted into the holes and then expanded via rolling. The tubes and tube sheets were joined using the gas tungsten inert welding method with a heat input of 0.036 kJ/mm and a shielding gas composed of either pure Ar or Ar + 2% N_2 without the filler metal. The chemical composition of the experimental HDSS alloy is presented in Table 1.

2.2. Thermodynamic calculation of phase diagram and equilibrium fractions of each phase

The commercial thermodynamic computing software, Thermo-Calc was used to perform the thermodynamic calculation and it should be stressed that such calculation gives the equilibrium state of system with the TCFE5-TCS Steels/Fe-alloys database [42,43]. The phase diagram and equilibrium fractions of each phase were calculated as a function of temperature for the HDSS alloy using the steel base TCFE5 available with a Thermo-Calc software package. Especially, in order to predict the formation of Cr_2N from the α-phase at high temperatures of a range of 1200–1400 °C, the mole fraction of each phase such as the α-phase, γ-phase and Cr_2N was calculated at 50 °C intervals.

2.3. Microstructural characterization

To observe the optical microstructures of the WM, HAZ, and base metal (BM) in the HDSS welds, the tubes were electrolytically etched using 10 wt.% potassium hydroxide solution. Volume fractions of α and γ-phases were calculated using the manual point-count method of according to the ASTM E562-02 [44]. The magnification of the micrograph was 500× and the grid size (number of points) was 25. Any points that fell on the boundary were counted as half (0.5). The chemical compositions of α and γ-phases were analyzed using the SEM–EDS (Table 2). Also, in order to accurately determine the fraction of α and γ-phases in the WM, quantitative phase analysis by means of XRD was performed on the HDSS welds. The XRD data was collected on a RINT-1400 diffractometer (40 kV/300 mA) equipped with a diffracted-beam monochromator, Cu Kα radiation, RINT-2000 vertical goniometer, $2\theta/\theta$ scan, sample spinning, divergence slit of 1°, a scatter slit of 1° and a receiving slit of 0.15 mm. The XRD measurements were carried out within a scan range of 30–120° (2θ) with a step size of 0.04° (2θ).

The Cr_2N precipitates formed in the HDSS welds during the welding process were analyzed using a thin-foil technique with TEM.

2.4. Double-loop electrochemical potentiokinetic reactivation (DL-EPR) test

The EPR technique is an electrochemical method for assessing sensitization that satisfies the demands for quantifiability and applicability [45]. The history of the EPR method was presented

Table 1
Chemical composition of the HDSS alloy (wt.%).

Alloy	C	Cr	Ni	Mo	W	Si	Mn	Ba	La	N	Ce	Fe	PREN[a]
HDSS	0.02	27.0	7.23	2.57	3.23	0.2	1.96	0.0006	0.0045	0.34	0.0137	Bal.	51

[a] PREN = wt.% Cr + 3.3 (Mo + 0.5 × wt.% W) + 30 × wt.% N.