Double-Loop Electrochemical Potentiokinetic Reactivation Method for Evaluating Intergranular Corrosion Susceptibility of 11Cr Ferritic Stainless Steel Postprint

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Date: 2023-03-19T00:00:00+00:00

Abstract

The characteristics of precipitates in 11Cr ferritic stainless steel 409L sensitized at 600 °C were investigated using transmission electron microscopy (TEM), energy-dispersive spectroscopy (EDS), and selected-area electron diffraction (SAED). The double-loop electrochemical potentiokinetic reactivation (DL-EPR) method was employed to evaluate the intergranular corrosion susceptibility of 409L steel. By studying the effects of scanning rate, electrolyte composition, and electrolyte temperature on the test results, the DL-EPR method was optimized, and this optimized method was used to investigate the influence of sensitization treatment on the intergranular corrosion susceptibility of 409L steel. The results indicate that intergranular corrosion in sensitized 409L steel occurs due to M23C6 precipitation along grain boundaries. Under optimized conditions, the DL-EPR method can quantitatively evaluate the intergranular corrosion susceptibility of 409L steel with good repeatability. With increasing sensitization treatment time, the amount of M23C6 precipitated along grain boundaries increases, and the intergranular corrosion susceptibility is correspondingly enhanced.

Full Text

Preamble

Acta Metallurgica Sinica
Vol. 51, No. 11, November 2015, pp. 1349-1355

Evaluation of Intergranular Corrosion Susceptibility of 11Cr Ferritic Stainless Steel by DL-EPR Method

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Supported by: National Natural Science Foundation of China (Nos. 51131008 and 51134010), National Key Technology Support Program (No. 2012BAE04B00), and Doctoral Fund of Ministry of Education of China (No. 20120071110013)

Received: February 18, 2015; Revised: April 19, 2015

DOI: 10.11900/0412.1961.2015.00117

Abstract

Ferritic stainless steel (FSS) containing 11%~13% Cr with low carbon and nitrogen exhibits excellent comprehensive performance and can be widely applied in automobile exhaust systems, containers, buses, and other fields. Among these materials, 409L steel containing 11% Cr has been increasingly used for tail pipes in the cold-end parts of automotive exhaust systems due to its good corrosion resistance and moderate price. However, improper heat treatments and welding operations during the manufacturing process for these tail pipes cause the precipitation of detrimental phases such as carbides and nitrides, which reduces resistance to intergranular corrosion (IGC) due to the formation of Cr-depleted zones at grain boundaries. In this work, the precipitates at grain boundaries of 409L steel aged at 600 °C were investigated using transmission electron microscopy (TEM), energy-dispersive spectroscopy (EDS), and selected-area electron diffraction (SAED). The double-loop electrochemical potentiokinetic reactivation (DL-EPR) method was extended to evaluate the IGC susceptibility of 409L steel. The operating conditions of the DL-EPR test for 409L steel were optimized by investigating the influences of key test parameters, including scanning rate, solution composition, and solution temperature. The experimental results showed that IGC in aged 409L steel occurred due to the precipitation of M23C6 along grain boundaries. The optimized DL-EPR test could quantitatively evaluate the IGC susceptibility of 409L steel with high reproducibility. With increasing aging time, more M23C6 precipitated along grain boundaries, which resulted in greater susceptibility to IGC.

Keywords: 11Cr ferritic stainless steel; double-loop electrochemical potentiokinetic reactivation; intergranular corrosion; M23C6

Introduction

Low-chromium ferritic stainless steel refers to ferritic stainless steel with Cr content between 11% and 13% [1–3]. With the application of argon-oxygen decarburization (AOD) and vacuum oxygen decarburization (VOD) technologies, along with the addition of stabilizing elements, the C and N contents in low-chromium ferritic stainless steel have been significantly reduced, substantially improving its corrosion resistance, mechanical properties, and weldability [4]. Furthermore, because low-chromium ferritic stainless steel contains less Cr and no Ni, its alloy cost is relatively low, leading to widespread applications in automotive exhaust systems, freight car bodies, containers, pipelines, and other fields [5–7]. Among these materials, 409L ferritic stainless steel containing 11% Cr has been increasingly used for manufacturing tail pipes in the cold-end sections of automotive exhaust systems due to its good corrosion resistance and moderate price [8,9]. However, improper heat treatment and welding processes during tail pipe manufacturing can cause extensive precipitation in 409L steel, which significantly affects its corrosion performance, particularly intergranular corrosion. While researchers have conducted in-depth studies on the effects of precipitates on intergranular corrosion in medium- and high-chromium stainless steels [10–13], investigations on low-chromium ferritic stainless steels remain very limited. For 409L steel specifically, its low C and Cr contents result in different precipitate types compared to those in medium- and high-chromium stainless steels [14,15]. Therefore, it is necessary to identify the types of precipitates, elucidate the mechanisms of intergranular corrosion, and investigate the relationship between precipitate content and sensitization treatment to clarify the effects of sensitization on the intergranular corrosion performance of 409L steel, thereby providing theoretical foundations and technical references for its production and application.

Traditional methods for evaluating intergranular corrosion susceptibility in stainless steel are primarily based on testing methods proposed in references [14,16,17] and are applicable to stainless steels with Cr content between 17% and 29% [18]. These methods suffer from several major drawbacks: difficulty in quantitatively assessing the degree of intergranular corrosion susceptibility, low sensitivity, long testing times, and destructive nature [19–21]. For low-chromium ferritic stainless steels, the highly aggressive solutions used in these methods cause severe uniform corrosion, making them unsuitable for evaluating intergranular corrosion susceptibility. In contrast, the double-loop electrochemical potentiokinetic reactivation (DL-EPR) method enables rapid, non-destructive, and quantitative detection of intergranular corrosion susceptibility in stainless steels. The principle relies on the relationship between the passivation-reactivation characteristics of stainless steel and the content of major alloying elements in the passive film and its properties. In the passive state, the morphology and structure of the passive film depend largely on the

Cr and Mo contents in the solid solution. Under specific electrolyte conditions and applied potentials, a complete and dense passive film forms on the steel surface, whereas sensitized specimens form incomplete passive films due to Cr depletion at grain boundaries [22–25]. When the applied potential is scanned back to the reactivation region, the incomplete passive film corrodes preferentially, resulting in increased reactivation current, which can be used to assess the degree of sensitization [26]. Chen and Hu [27] applied this method in developing a detector for intergranular corrosion testing of stainless steels, successfully implementing it for on-site non-destructive testing. The DL-EPR method was initially applied to evaluate intergranular corrosion susceptibility in 300-series austenitic stainless steels [28,29]. Subsequently, Mignone et al. [30] and Lee [31] successfully adapted it for high-chromium alloy 800 and medium-chromium ferritic stainless steels AISI 430 and 444 by adjusting test parameters. However, it was not until 1992 that the DL-EPR method was reported for studying intergranular corrosion susceptibility in low-chromium ferritic stainless steels [18]. With the expanding application of low-chromium ferritic stainless steels and increasing intergranular corrosion failure incidents, using the DL-EPR method to study their intergranular corrosion susceptibility has significant practical importance. Currently, few reports exist on applying the DL-EPR method to study the intergranular corrosion susceptibility of 409L steel for automotive exhaust systems, and the optimal conditions for this method remain unclear.

Therefore, the objective of this work is to establish the optimal conditions for DL-EPR testing of 409L steel and to qualitatively and quantitatively investigate changes in its intergranular corrosion susceptibility after sensitization at 600 °C.

Experimental Methods

The experimental material was 11Cr ferritic stainless steel 409L with the following chemical composition (mass fraction, %): C 0.011, Cr 11.55, Ni 0.15, Ti 0.23, Nb 0.01, N 0.0063, and Fe balance. The steel was cut into specimens measuring 10 mm × 10 mm × 1 mm, solution-treated at 1200 °C for 1 h, water-quenched, and then sensitized at 600 °C for 0.5, 4, and 10 h. All heat treatments were performed in pure N2. Electrical leads were attached to the non-working surfaces of the specimens, which were then encapsulated in epoxy resin, exposing a test area of 1 cm^2. After sealing the working electrode, the working surface was ground sequentially with water-abrasive paper, cleaned with distilled water, ethanol, and acetone, and dried.

DL-EPR tests were conducted using a CHI660B electrochemical workstation with a standard three-electrode system: a Pt auxiliary electrode, a saturated calomel reference electrode (SCE), and a 409L steel working electrode. The working electrode was immersed in 0.5% H2SO4 solution with varying mass fractions of KSCN (potassium thiocyanate, a depolarizer). The potential was scanned anodically from the corrosion potential at different scanning rates. When the passivation potential reached 700 mV, the scan direction was reversed at the same rate back to the corrosion potential, yielding the maximum current in the forward scan (Ia) and the maximum current in the reverse scan (Ir). The ratio of Ir to Ia (Ra) was used to characterize the material's intergranular corrosion susceptibility, with higher Ra values indicating greater susceptibility [32]. For each sensitization condition, two parallel specimens were prepared, and each was tested three times. The average Ra value from all tests on the two parallel specimens was taken as the Ra for that sensitization condition to reduce experimental error. The corrosion morphology was observed using a 4XGE optical microscope (OM), and changes in grain boundary composition before and after heat treatment were examined using energy-dispersive spectroscopy (EDS) on a JEOL-2100F transmission electron microscope (TEM). Thermo-Calc software was used for thermodynamic calculations to obtain the equilibrium phase diagram of 409L steel.

2.1 Heat Treatment Precipitates

[Figure 1: see original paper] shows the equilibrium phase fractions in 409L steel as a function of temperature, calculated using Thermo-Calc software. TiC begins to decompose at 950 °C, reaching 25.5% decomposition at 1200 °C, while TiN remains stable [5]. Therefore, solution treatment at 1200 °C generates a certain amount of free C atoms, resulting in supersaturated C in the matrix after water quenching. Due to the low solubility of C in ferritic stainless steel [18,33], sensitization at 600 °C causes supersaturated C atoms to diffuse to grain boundaries and combine with Cr to form chromium carbides.

[Figure 2: see original paper] presents TEM images, EDS analysis, and SAED patterns of grain boundaries in 409L steel before and after sensitization at 600 °C for 4 h. As shown in [Figure 2: see original paper]a, the as-received 409L steel exhibits no intergranular corrosion susceptibility, with no precipitates at grain boundaries. After sensitization for 4 h ([Figure 2: see original paper]b and c), precipitates form at grain boundaries. EDS analysis ([Figure 2: see original paper]d) indicates these precipitates are compounds of C, Cr, and Fe, while the SAED pattern ([Figure 2: see original paper]e) further confirms them as M23C6. After sensitization at 600 °C, M23C6 precipitates along grain boundaries, consuming large amounts of Cr in the vicinity. Since Cr in the matrix cannot diffuse to grain boundaries quickly enough at this temperature [18], Cr-depleted zones form near grain boundaries, creating an active-passive galvanic corrosion cell with the grains as cathodes and the Cr-depleted zones as anodes. This leads to severe anodic dissolution in the Cr-depleted zones, resulting in intergranular corrosion [14].

2.2 Effect of KSCN Concentration on DL-EPR Test Results

[Figure 3: see original paper] shows DL-EPR test results for 409L steel in 0.5% H2SO4 solution at 30 °C with a scanning rate of 1.667 mV/s and KSCN mass fractions of 0.0001%, 0.002%, 0.01%, and 0.1%. The DL-EPR test's ability to reveal intergranular corrosion susceptibility depends on KSCN concentration;

low concentrations are unfavorable for revealing intergranular corrosion [18]. At very low concentrations, the reverse scan peak is not prominent, resulting in low Ir values, while the forward scan peaks (Ia) for different sensitized specimens show small differences. Consequently, when KSCN concentration is 0.0001%, the Ra values obtained from DL-EPR tests for various sensitized conditions show little distinction. At KSCN concentrations of 0.01% and 0.1%, the Ra values for the as-received 409L steel (which has no intergranular corrosion susceptibility) are 3.21% and 15.31%, respectively, failing to meet the DL-EPR test validity requirement that Ra for non-sensitized materials must be less than 1% [34]. Therefore, these two concentrations are unsuitable as test parameters. Only at a KSCN concentration of 0.002% does the as-received 409L steel exhibit Ra < 1%, with significant differences in Ra among various sensitized specimens. Thus, to effectively characterize the intergranular corrosion susceptibility of different sensitized conditions, the optimal KSCN concentration was determined to be 0.002%.

2.3 Effect of Scanning Rate on DL-EPR Test Results

[Figure 4: see original paper] presents DL-EPR test results for 409L steel in 0.5% H2SO4 + 0.002% KSCN solution at 30 °C at scanning rates of 0.5, 1.667, 2.5, and 5 mV/s. The scanning rate has almost no effect on Ra for as-received 409L steel specimens due to their lack of intergranular corrosion susceptibility, but significantly affects Ra for sensitized specimens. As the scanning rate increases, Ra for sensitized specimens decreases rapidly. At 5 mV/s, the difference in Ra among various sensitized conditions becomes very small because the rapid scan rate results in insufficient dissolution of Cr-depleted zones during the reverse scan. Since Ir corresponds to dissolution of Cr-depleted zones, the Ir values show little variation, while the Ia values during the forward scan are similar, leading to small differences in Ra. At very low scanning rates (0.5 mV/s), although the Ra differences are more pronounced, severe uniform corrosion occurs due to prolonged immersion, making 0.5 mV/s unsuitable as a test parameter. At a scanning rate of 1.667 mV/s, the distinction in Ra is more evident than at 2.5 mV/s, making 1.667 mV/s the preferred scanning rate for DL-EPR testing.

2.4 Effect of Solution Temperature on DL-EPR Test Results

[Figure 5: see original paper] shows DL-EPR test results for 409L steel in 0.5% H2SO4 + 0.002% KSCN solution at a scanning rate of 1.667 mV/s and temperatures of 20, 25, 30, and 40 °C. Solution temperature has minimal effect on Ra for as-received 409L steel specimens but significantly affects sensitized specimens. As temperature increases, Ra increases and the differences among various sensitized conditions become more pronounced. However, at lower temperatures (20 and 25 °C), the Ra differences are small. At 40 °C, the Ra for the as-received specimen is 1.01%, which contradicts the DL-EPR test validity requirement that Ra for non-sensitized materials must be less than 1%. At 30 °C, the Ra values for different sensitized conditions show significant differences, and the as-received 409L steel exhibits Ra < 1%, making 30 °C the selected test condition.

Based on the above discussion, the optimal conditions for DL-EPR testing of 409L steel are: solution composition of 0.5% H2SO4 + 0.002% KSCN, scanning rate of 1.667 mV/s, and solution temperature of 30 °C. Under these conditions, repeated tests on 409L steel specimens sensitized at 600 °C for 0.5 and 4 h showed minimal Ra variation, demonstrating good reproducibility of the DL-EPR test.

[Figure 6: see original paper] shows DL-EPR curves for 409L steel under optimal conditions. The curves exhibit a long passivation region (-0.3 to 0.7 V) with passivation currents approaching zero, while the maximum current in the forward activation scan (Ia) is on the order of 10^{-2} A/cm^2, independent of intergranular corrosion susceptibility. For the maximum reactivation current in the reverse scan (Ir), there is a substantial difference between as-received and sensitized specimens, with the former being significantly lower. This occurs because as-received specimens essentially lack Cr-depleted zones at grain boundaries, while sensitized specimens exhibit obvious Cr-depleted zones where the passive film formed at grain boundaries is extremely unstable and breaks down during the reverse potential scan, resulting in higher Ir values.

presents DL-EPR test results for 409L steel sensitized at 600 °C for different durations under optimal conditions. As sensitization time increases, Ra increases, indicating enhanced intergranular corrosion susceptibility. This is because longer sensitization times lead to increased M23C6 precipitation at grain boundaries, resulting in more numerous and wider Cr-depleted zones. Consequently, intergranular corrosion susceptibility increases, the reverse scan peak rises during DL-EPR testing (corresponding to increased Ir), while Ia remains relatively similar, leading to higher Ra values.

[Figure 7: see original paper] shows optical micrographs of 409L steel after DL-EPR testing under optimal conditions. As shown in [Figure 7: see original paper]a, the as-received 409L steel surface shows no intergranular corrosion, indicating the absence of Cr-depleted zones and consistent with the observation from [Figure 2: see original paper]a that no Cr-rich carbides precipitate at grain boundaries. This confirms the reliability of using the DL-EPR method under optimal conditions to evaluate the intergranular corrosion susceptibility of 409L steel. [Figure 7: see original paper]b–d reveal that solution treatment at 1200 °C significantly enlarges the grain size of 409L steel to the order of 100 m, which increases intergranular corrosion susceptibility. Furthermore, sensitization at 600 °C causes M23C6 precipitation at grain boundaries. As sensitization time increases, more M23C6 precipitates form, leading to more numerous and wider Cr-depleted zones and consequently more severe intergranular corrosion morphologies. This trend aligns with the Ra values shown in , further demonstrating that DL-EPR testing under optimal conditions can quantitatively evaluate the intergranular corrosion susceptibility of 409L steel.

Conclusions

1. The intergranular corrosion of 409L steel after solution treatment at 1200 °C and sensitization at 600 °C is caused by M23C6 precipitation along grain boundaries.
2. The optimal conditions for evaluating the intergranular corrosion susceptibility of 409L steel by DL-EPR testing are: solution composition of 0.5% H2SO4 + 0.002% KSCN, solution temperature of 30 °C, and scanning rate of 1.667 mV/s. Under these conditions, DL-EPR testing can quantitatively evaluate the intergranular corrosion susceptibility of 409L steel with good reproducibility.
3. As sensitization time increases, more M23C6 precipitates along grain boundaries, leading to enhanced intergranular corrosion susceptibility.

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