Effect of Grain Boundary Engineering on Improving the Intergranular Corrosion Resistance of 304 Austenitic Stainless Steel Weld Heat-Affected Zone Postprint

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Abstract

Through grain boundary engineering (GBE) processing involving 5% cold rolling deformation and annealing at 1100℃ for 30 min, the proportion of low-Σ CSL grain boundaries in 304 austenitic stainless steel can be increased to over 75% (according to the Palumbo-Aust criterion), and a microstructure consisting of large-scale "clusters of grains with Σ3^n orientation relationships" is formed. Samples were welded using gas tungsten arc welding, and microstructure characterization and corrosion resistance testing were performed on the heat-affected zone of the welded samples. The results demonstrate that GBE-processed 304 austenitic stainless steel exhibits good grain boundary network stability, the weld heat-affected zone still maintains a high proportion of coincidence site lattice grain boundaries, and the grain size does not increase significantly. In both intergranular corrosion experiments and EPR tests, the sensitized zone of the HAZ in GBE samples showed superior corrosion resistance, thus indicating that grain boundary engineering can effectively improve the intergranular corrosion resistance of the weld heat-affected zone in 304 austenitic stainless steel.

Full Text

Abstract

The heat-affected zone (HAZ) produced by welding in stainless steel exhibits higher susceptibility to intergranular corrosion, which is attributed to chromium depletion induced by grain-boundary carbide precipitation. Grain boundary engineering can be used to control the grain boundary structure, which significantly influences carbide precipitation and the associated chromium depletion,

and hence affects the susceptibility to intergranular corrosion. The grain boundary network in 304 austenitic stainless steel can be controlled by grain boundary engineering (GBE) through 5% cold rolling and subsequent annealing at 1100 °C for 30 min. The total length proportion of $\Sigma 3^n$ coincidence site lattice (CSL) boundaries was increased to more than 75%, and a large-size, highly-twinned grain-cluster microstructure was formed through GBE treatment. Specimens were welded by gas tungsten arc welding, after which the microstructure and corrosion resistance of the HAZ were characterized. The results show that the high proportion of low-Σ CSL boundaries and the optimum grain boundary character distribution remained stable in the HAZ of the grain boundary engineered stainless steel, and the grain size was nearly unchanged. The weld-decay region of GBE samples demonstrated better intergranular corrosion resistance during both the intergranular corrosion immersion experiment and electrochemical potentiokinetic reactivation (EPR) test. These results indicate that grain boundary engineering can effectively improve the intergranular corrosion resistance of the heat-affected zone in 304 austenitic stainless steel.

Keywords: 304 austenitic stainless steel, grain boundary engineering, heat-affected zone, intergranular corrosion, welding

Introduction

Austenitic stainless steels are widely used in petroleum, chemical, aerospace, and nuclear industries due to their excellent comprehensive properties [1]. Since they operate long-term in corrosive environments, they must possess not only adequate strength but also good corrosion resistance. However, during welding of austenitic stainless steels, certain regions in the weld heat-affected zone (HAZ) are heated to sensitization temperatures (600–1000 °C), where chromium-rich carbides easily precipitate at grain boundaries, creating chromium-depleted zones near the boundaries and causing severe intergranular corrosion susceptibility [1–6]. This region is commonly referred to as the "HAZ sensitization zone" or weld-decay region [4–6]. To mitigate sensitization, carbon content can be reduced in austenitic stainless steels by using 304L low-carbon steel instead of conventional 304 steel, or by adding alloying elements such as Ti and Nb to form stable carbides [6].

In 1984, Watanabe [7] proposed the concept of grain boundary design, which subsequently evolved into the research field of "grain boundary engineering (GBE)" in the 1990s. Through appropriate deformation and annealing processes, the proportion of low-Σ CSL (coincidence site lattice [8], where low-Σ CSL refers to $\Sigma \leq 29$) grain boundaries can be significantly increased, optimizing their distribution and improving various grain-boundary-related properties [9–11]. GBE processing has been successfully applied to nickel-based alloys [12–14], lead-based alloys [15,16], and austenitic stainless steels [17–20].

304 austenitic stainless steel is a low stacking fault energy fcc metal. GBE methods can be used to increase the proportion of low-Σ CSL grain bound-

aries, suppress carbide precipitation, and improve intergranular corrosion resistance. Fang et al. [19] investigated the grain boundary character distribution of 304 austenitic stainless steel after various deformation and annealing treatments, finding that small cold rolling deformation (6%–10%) combined with long-duration annealing at 900 °C (24–96 h) could significantly increase the proportion of low-Σ CSL grain boundaries. Shimada et al. [20] reported that after cold rolling 5% and annealing 304 austenitic stainless steel at 927 °C for 72 h, the proportion of low-Σ CSL grain boundaries exceeded 80% (Brandon criterion [21]), and the intergranular corrosion rate decreased by approximately 75%. However, most reported processes for increasing low-Σ CSL grain boundaries in 304 stainless steel use annealing temperatures inconsistent with solution treatment temperatures.

In practical industrial applications, to obtain satisfactory mechanical and corrosion properties, 304 stainless steel typically requires solution treatment after forming, sometimes followed by stabilization aging treatment. Our previous work [17,18] investigated processes for increasing low-Σ CSL grain boundaries in 304 austenitic stainless steel through cold deformation and annealing at solution treatment temperatures. The results demonstrated that GBE processing can increase the proportion of low-Σ CSL grain boundaries and form a large-size "grain cluster with $\Sigma 3^n$ orientation relationships" microstructure. Since the annealing temperature matches the solution treatment temperature, this process can be effectively integrated with current production practices. This work investigates the welding of GBE-processed 304 austenitic stainless steel to examine how the special grain boundary network improves the intergranular corrosion resistance of the weld heat-affected zone.

Experimental Methods

The chemical composition of the 304 austenitic stainless steel used in this study was (mass fraction, %): Cr 18.31, Ni 8.75, Mn 1.18, Si 0.58, C 0.08, with Fe as the balance. The as-received 304 austenitic stainless steel was cut by wire electrical discharge machining into samples measuring 100 mm (length) × 40 mm (width) × 6 mm (thickness). Sample A was prepared by cold rolling to 50% reduction, annealing at 1100 °C for 60 min, and immediate water quenching as a solution-treated specimen. Sample B was prepared by cold rolling to 50% reduction, solution treatment at 1100 °C for 20 min, followed by GBE processing (5% room-temperature tensile deformation and annealing at 1100 °C for 30 min with water quenching).

The surfaces of the annealed samples were ground sequentially with 400, 1000, and 2000 grit sandpaper and mechanically polished. Electrolytic polishing was then used to prepare surfaces suitable for electron backscatter diffraction (EBSD) analysis. The electrolytic polishing solution consisted of 20% $HClO_4$ + 80% CH_3COOH (volume fraction), applied at 40 V DC for approximately 2 min. A CamScan Apollo-300 thermal field emission gun scanning electron microscope (SEM) equipped with an HKL-EBSD system was used for point-by-point scanning of the electrolytically polished surfaces with a step size of 4 m. This yielded the orientation of each point in the scanned surface area, allowing grain boundary types to be determined from the misorientation between adjacent grains. This work adopted the Palumbo-Aust criterion [22]: $\Delta \quad = 15^\circ\ \Sigma^{-5}/^{6}$ (where Δ refers to the maximum deviation angle between the experimentally measured CSL orientation relationship and the standard geometric CSL orientation relationship) to identify grain boundary types, with HKL-Channel5 software automatically calculating the length percentages of different boundary types. Table 1 presents the processing parameters and grain boundary character distribution (GBCD) statistics for the samples.

Gas tungsten arc welding (GTA-W) was performed on the samples without filler material to avoid contamination, using a single welding pass. To ensure identical welding speeds, samples A and B were welded together in the configuration shown in [Figure 1: see original paper] at a welding speed of approximately 6 cm/min. After welding and air cooling, the weld and adjacent regions were extracted by wire cutting. The welded sample surfaces were ground with sandpaper and mechanically polished. After etching with a solution of 10% HNO_3 + 3% HF + 87% H_2O (volume fraction), the microstructures of different regions on the welded surfaces were observed by optical microscopy (OM). The welded surfaces were electrolytically polished, and orientation imaging microscopy (OIM) maps of different regions were obtained using EBSD.

The location of the HAZ sensitization zone was identified through microstructural characterization of the welded samples. Corresponding HAZ sensitization regions from samples A and B (designated A-W and B-W, respectively) were extracted with dimensions of 10 mm × 5 mm × 3 mm for intergranular corrosion testing and electrochemical potentiokinetic reactivation (EPR) measurements. Intergranular corrosion experiments were conducted at room temperature using the same etching solution as for metallographic examination. Samples were suspended in the corrosion solution with all surfaces exposed. At intervals, samples were removed, cleaned, weighed (to 0.1 mg precision), and examined by OM and SEM. During the first 12 h, samples were removed every 3 h; subsequently, they were removed every 12 h, for a total immersion time of 96 h.

According to ASTM G108-94 standard, the EPR method was used to evaluate the degree of sensitization [23–27] using a Zannium electrochemical workstation. The EPR method measures the reactivation polarization curve of a specimen in a specific electrolyte (0.5 mol/L H_2SO_4 + 0.01 mol/L KSCN) and calculates the reactivation ratio, which depends on the degree of sensitization. A higher reactivation ratio indicates greater sensitization and poorer intergranular corrosion resistance. Comparative tests were performed on both the welded surfaces and cross-sections of samples A-W and B-W, which were encapsulated in epoxy resin with a test area of 10 mm × 3 mm and a scan rate of 1 mV/s.

Results and Discussion

2.1 Microstructural Characteristics of Grain Boundary Networks After GBE Processing

[Figure 2: see original paper] presents OIM maps of different grain boundary types in samples A and B. The GBE-processed sample B exhibited a low-Σ CSL grain boundary proportion of 75.6%, compared to only 45.0% in sample A (Table 1). This difference arises because multiple twinning was fully developed during recrystallization in sample B, forming numerous $\Sigma 3^n$ boundaries [17,18]. These boundaries interconnected to form many triple junctions such as Σ3-Σ3-Σ9 and Σ3-Σ9-Σ27, creating large-size "grain clusters with $\Sigma 3^n$ orientation relationships" (hereinafter referred to as grain clusters), exemplified by clusters C1 and C2 in [Figure 2: see original paper]b. The clusters were typically separated by random boundaries. Grain size was measured using the equivalent circle diameter method, counting twins as grains. Sample A had a grain size of 24.3 m, while sample B had a grain size of 28.1 m. Although the grain sizes were similar, the grain cluster sizes differed significantly between the two samples.

2.2 Microstructure After Welding

[Figure 3: see original paper] shows the macroscopic microstructures of welded samples A and B after corrosion. The welded surfaces can be divided into three distinct regions: the weld (region 1), the weld heat-affected zone (regions 2 and 3), and the base material (region 4). The HAZ can be further subdivided into a grain-coarsened area (region 2) and a sensitization zone (region 3). The grain-coarsened area was approximately 4 mm wide, and the sensitization zone was about 4 mm wide. Sample A exhibited a distinct HAZ sensitization zone approximately 4 mm from the weld, identified by a darker corroded surface distinguishing it from other microstructural regions. In contrast, sample B showed no obvious HAZ sensitization zone, with minimal difference in appearance near the weld.

[Figure 4: see original paper] presents OIM maps showing the distribution of different grain boundary types in the microstructures of welded samples A and B. Sample B’ s HAZ (regions 2 and 3) contained abundant $\Sigma 3^n$ boundaries, similar to the base material, and retained the characteristic microstructure of large-size grain clusters with $\Sigma 3^n$ orientation relationships. According to automatic EBSD software statistics, the proportions of low-Σ CSL boundaries in the grain-coarsened area and sensitization zone of sample B were 70.4% and 72.3%, respectively—values comparable to the base material and significantly higher than the corresponding regions in sample A, as shown in [Figure 5: see original paper]a. The grain sizes in the grain-coarsened area and sensitization zone of sample B were 32.2 m and 27.9 m, respectively, also comparable to the base material ([Figure 5: see original paper]b). These results demonstrate that sample B’ s HAZ grain boundary network exhibited excellent stability, maintaining the grain boundary character distribution of the base material.

2.3.1 Intergranular Corrosion

During corrosion, intergranular corrosion in the HAZ sensitization zone causes grain dropping and mass loss. The surface microstructures after 48 h of corrosion are shown in [Figure 6: see original paper]. Sample A-W exhibited a clear sensitization zone, with SEM images at higher magnification ([Figure 6: see original paper]c) revealing severe intergranular corrosion, extensive grain dropping, and corrosion penetration to significant depths. In contrast, sample B-W showed no visible HAZ sensitization zone on the surface, and corresponding high-magnification SEM images ([Figure 6: see original paper]d) revealed no grain dropping or obvious intergranular corrosion. The mass loss results in [Figure 7: see original paper] confirm that sample B-W had a lower corrosion rate than sample A-W. This improvement is attributed to the high proportion of low-Σ CSL boundaries in the HAZ sensitization zone of sample B-W, where chromium depletion due to carbide precipitation is less severe [28,29], resulting in better resistance to intergranular corrosion.

During welding, the HAZ sensitization zone experiences a short heating time in the sensitization temperature range, so it does not become fully sensitized through the entire thickness. [Figure 8: see original paper]a and b show cross-sectional SEM images of samples A-W and B-W after 96 h of corrosion. Sample B-W maintained good surface integrity, while sample A-W exhibited severe intergranular corrosion. The corrosion depth in sample A-W was greatest at the mid-thickness position and gradually decreased toward the edges, forming an arc-shaped profile. This indicates that although severe intergranular corrosion occurred, the HAZ sensitization zone was not fully sensitized through the entire thickness, which explains why the mass loss difference between samples A-W and B-W was not more pronounced. Additionally, the HAZ sensitization zone samples A-W and B-W contained portions of grain-coarsened area or base material, which would also reduce the difference in mass loss. Nevertheless, the observed difference clearly demonstrates that GBE-processed 304 stainless steel exhibits significantly improved intergranular corrosion resistance in the HAZ after welding.

2.3.2 EPR Testing

The EPR method measures the reactivation current (I) and activation current (I), using their ratio—the reactivation ratio (I /I × 100%)—as an indicator of sensitization degree. Based on the test curves ([Figure 9: see original paper]), the calculated sensitization degrees for sample A-W were 0.34% on the welded surface and 0.18% on the cross-section, while for sample B-W they were 0.18% and 0.14%, respectively. These results show that sample B-W had lower sensitization than sample A-W on both the welded surface and cross-section, with a particularly large difference on the surface, indicating superior intergranular corrosion resistance. The higher sensitization on the welded surface compared to the cross-section is consistent with the short heating time in the sensitization temperature range during welding, which results in incomplete sensitization through the thickness. Consequently, the cross-section exhibits lower sensitization and a correspondingly lower reactivation ratio.

Conclusions

1. GBE-processed 304 austenitic stainless steel exhibits good grain boundary network stability, maintaining a high proportion of low-Σ CSL boundaries in the weld heat-affected zone without significant grain growth.
2. In intergranular corrosion experiments, GBE-processed samples demonstrated superior intergranular corrosion resistance in the HAZ sensitization zone compared to untreated samples.
3. EPR testing revealed that the sensitization degree on both the welded surface and cross-section of GBE-processed samples was lower than that of untreated samples in the corresponding regions.

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Note: Figure translations are in progress. See original paper for figures.