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% tensile deformation and annealing at 1100 °C for 30 min, the proportion of low-Σ coincidence site lattice (CSL) grain boundaries in 304 austenitic stainless steel was increased to over 75% (Palumbo-Aust criterion), forming a large-scale microstructure of "grain clusters with Σ3^n orientation relationships". Samples were welded using gas tungsten arc welding, and microstructural characterization and corrosion resistance testing were performed on the HAZ region of the welded samples. The results demonstrate that GBE-processed 304 austenitic stainless steel exhibits good grain boundary network stability, maintaining a high proportion of low-Σ CSL grain boundaries in the HAZ region without significant grain growth. In intergranular corrosion immersion tests and electrochemical potentiokinetic reactivation (EPR) tests, the sensitized zone in the HAZ of GBE-processed samples showed superior corrosion resistance, 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

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

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Abstract

The heat-affected zone (HAZ) produced by welding in stainless steel exhibits higher susceptibility to intergranular corrosion, which is attributed to Cr 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 Cr depletion, and hence the susceptibility to intergranular corrosion. The grain boundary network in 304 austenitic stainless steel can be controlled through grain boundary engineering (GBE) involving 5% tensile deformation and subsequent annealing at 1100 °C for 30 min. This treatment increased the total length proportion of $\Sigma 3^n$ coincidence site lattice (CSL) boundaries to more than 75% and formed a large-size, highly-twinned grain-cluster microstructure. Specimens were welded by gas tungsten arc-welding, after which the microstructure and corrosion resistance of the HAZ were characterized. The results showed 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, with no significant grain growth. During intergranular corrosion immersion experiments and electrochemical potentiokinetic reactivation (EPR) testing, the weld-decay region of GBE samples demonstrated superior corrosion resistance, indicating that grain boundary engineering can effectively improve the intergranular corrosion resistance of the heat-affected zone in 304 austenitic stainless steel.

KEY WORDS 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 these materials operate in corrosive environments for extended periods, 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 Cr-rich carbides readily precipitate at grain boundaries, creating Cr-depleted zones that cause 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, the carbon content can be reduced in austenitic stainless steels by using 304L low-carbon steel instead of conventional 304 stainless steel, or by adding alloying elements such as Ti and Nb to stabilize carbon through carbide formation [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 $\Sigma \leq 29$) 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 material whose low-Σ CSL boundary proportion can be increased through GBE to inhibit carbide precipitation and enhance intergranular corrosion resistance. Fang et al. [19] investigated the grain boundary character distribution in 304 austenitic stainless steel after various deformation and annealing treatments, demonstrating that small cold rolling deformations (6%-10%) combined with long-duration annealing at 900 °C (24-96 h) could effectively increase the low-Σ CSL boundary proportion. Shimada et al. [20] reported that after cold rolling 304 austenitic stainless steel by 5% and annealing at 927 °C for 72 h, the low-Σ CSL boundary proportion exceeded 80% (according to the Brandon criterion [21]), and the intergranular corrosion rate decreased by approximately 75%. However, many reported processes for increasing low-Σ CSL boundaries in 304 stainless steel involve annealing temperatures that differ from solution treatment temperatures. In practical industrial applications, solution treatment is typically required after forming to obtain satisfactory mechanical and corrosion properties, sometimes followed by stabilization aging treatments. Our previous work [17,18] investigated processes for increasing low-Σ CSL boundaries in 304 austenitic stainless steel through cold deformation and annealing at solution treatment temperatures. The results showed that GBE processing could increase the low-Σ CSL boundary proportion and form a large-size "grain cluster with $\Sigma 3^n$ orientation relationships" microstructure. Since the annealing temperature coincides with the solution treatment temperature, this process can be effectively integrated with existing production routes. This study investigates the effect of this special grain boundary network on improving the intergranular corrosion resistance of the weld heat-affected zone in 304 austenitic stainless steel after GBE processing and welding.

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 balance. The as-received material was cut by wire electrical discharge machining into specimens measuring 100 mm (length) × 40 mm (width) × 6 mm (thickness). These were cold-rolled by 50% and then solution-treated at 1100 °C for 60 min followed by water quenching, designated as specimen A. Other specimens were cold-rolled by 50%, solution-treated at 1100 °C for 20 min, and then subjected to GBE processing (5% room-temperature tensile deformation followed by annealing at 1100 °C for 30 min with water quenching), designated as specimen B. The processing parameters for specimens A and B are summarized in .

The surfaces of annealed specimens were sequentially ground with 400, 1000, and 2000 grit sandpaper and mechanically polished. Electrolytic polishing was then performed to prepare surfaces suitable for electron backscatter diffraction (EBSD) analysis. The electrolyte 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 with a step size of 4 m to obtain orientation data across the specimen surfaces. Grain boundary types were determined from the misorientation between adjacent grains. The Palumbo-Aust criterion [22] ($\Delta \quad = 15° \Sigma^{-5}/^{6}$, where Δ is the maximum deviation angle between the experimentally measured CSL orientation relationship and the ideal geometric CSL orientation relationship) was used to identify boundary types, with HKL-Channel5 software automatically calculating the length percentages of different boundary types.

Specimens were welded by gas tungsten arc-welding (GTA-W) without filler metal to avoid contamination, using a single pass. To ensure identical welding speeds, specimens 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 air cooling, the weld and adjacent regions were sectioned by wire electrical discharge machining. The welded surfaces were ground and mechanically polished, then etched with a solution of 10% HNO_3 + 3% HF + 87% H_2O (volume fraction) for optical microscopy (OM) examination of different regions. The welded surfaces were also electrolytically polished for EBSD orientation imaging microscopy (OIM).

Based on microstructural characterization, the HAZ sensitization zones were identified in both specimens. Corresponding regions from specimens 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 tests were conducted at room temperature using the same etching solution. Specimens were suspended in the corrosive solution with all surfaces exposed. At intervals, specimens were removed, cleaned, and weighed (to 0.1 mg precision), with surface morphology examined by OM and SEM. During the first 12 h, specimens 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 sensitization degree [23-27] using a Zannium electrochemical workstation. This method measures the reactivation polarization curve of stainless steel in a specific electrolyte (0.5 mol/L H_2SO_4 + 0.01 mol/L KSCN) and calculates the reactivation ratio. The reactivation ratio depends on the degree of sensitization, which reflects intergranular corrosion resistance—higher reactivation ratios indicate greater sensitization and poorer corrosion resistance. EPR tests were performed on both the welding surface and cross-section of specimens A-W and B-W. Samples were encapsulated in epoxy resin with a test area of 10 mm × 3 mm, scanned at 1 mV/s.

Results and Discussion

2.1 Microstructural Characteristics of Grain Boundary Networks After GBE Processing

presents the grain boundary character distribution and grain sizes of specimens A and B. The OIM maps in [Figure 2: see original paper] show different types of grain boundaries. The GBE-processed specimen B exhibited a low-Σ CSL boundary proportion of 75.6%, compared to only 45.0% in specimen A. This increase resulted from the full development of multiple twinning during recrystallization, forming numerous $\Sigma 3^n$ boundaries [17,18]. These boundaries interconnected to create many triple junctions such as Σ3-Σ3-Σ9 and Σ3-Σ9-Σ27, forming 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 separate grains. The average grain size was 24.3 m for specimen A and 28.1 m for specimen B—similar values. However, the grain cluster sizes differed substantially, at 51.1 m and 124.4 m, respectively ().

2.2 Microstructure After Welding

[Figure 3: see original paper] shows the macroscopic microstructure of welded specimens A and B after etching. The welded surface microstructure 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 weld-decay region (region 3), each approximately 4 mm wide. In specimen A, a distinct HAZ sensitization zone was observed 4 mm from the weld, appearing darker after corrosion. In contrast, specimen B showed no obvious HAZ sensitization zone, with minimal change in appearance near the weld.

[Figure 4: see original paper] presents OIM maps of different grain boundary types in various regions of welded specimens A and B. The HAZ (regions 2 and 3) in specimen B retained a high proportion of $\Sigma 3^n$ boundaries and the characteristic large-size grain cluster microstructure, similar to the base material. According to automated EBSD statistics, the low-Σ CSL boundary proportions in the grain-coarsened area and weld-decay region of specimen B were 70.4% and 72.3%, respectively—comparable to the base material and significantly higher than the corresponding regions in specimen A ([Figure 5: see original paper]a). The grain sizes in these regions were 32.2 m and 27.9 m, respectively, also similar to the base material ([Figure 5: see original paper]b). These results demonstrate excellent stability of the grain boundary network in the HAZ of GBE-processed specimen B, which maintained the base material’ s grain boundary character distribution.

2.3 Effect of Grain Boundary Network Distribution on Intergranular Corrosion Performance in the HAZ Sensitization Zone

2.3.1 Intergranular Corrosion During corrosion, intergranular corrosion in the HAZ sensitization zone causes grain dropping and mass loss. [Figure 6: see original paper] shows the surface morphology after 48 h of corrosion. In specimen A-W, the sensitization zone is clearly visible ([Figure 6: see original paper]a), with SEM examination ([Figure 6: see original paper]c) revealing severe intergranular corrosion, extensive grain dropping, and significant penetration depth. In contrast, specimen B-W showed no visible sensitization zone ([Figure 6: see original paper]b), and corresponding 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 specimen B-W exhibited a lower corrosion rate than A-W. This improvement is attributed to the high proportion of low-Σ CSL boundaries in the HAZ sensitization zone of B-W, where Cr depletion due to carbide precipitation is less pronounced [28,29], resulting in better intergranular corrosion resistance.

During welding, the HAZ sensitization zone experiences only brief heating in the sensitization temperature range, so complete sensitization through the thickness does not occur. [Figure 8: see original paper] shows cross-sectional SEM images after 96 h of corrosion. Specimen B-W maintained good surface integrity, while specimen A-W exhibited severe intergranular corrosion. The corrosion depth in A-W was greatest at the mid-thickness position beneath the weld surface, decreasing toward the edges in an arc-shaped profile. Although severe intergranular corrosion occurred in A-W, incomplete sensitization through the thickness limited the mass loss difference between A-W and B-W. Additionally, the tested samples contained portions of the grain-coarsened area and base material, further reducing the measured difference. Nevertheless, the results clearly demonstrate that GBE processing significantly improves the intergranular corrosion resistance of the HAZ in welded 304 stainless steel.

2.3.2 EPR Testing The EPR method measures the reactivation current (I) and activation current (I), with the reactivation ratio (I /I × 100%) indicating the degree of sensitization. Based on the test curves in [Figure 9: see original paper], the sensitization degrees of specimen A-W were 0.34% (welding surface) and 0.18% (cross-section), while those of specimen B-W were 0.18% (surface) and 0.14% (cross-section). Specimen B-W exhibited lower sensitization than A-W in both locations, particularly on the welding surface where the difference was substantial. This confirms the superior intergranular corrosion resistance of the GBE-processed specimen. The higher sensitization on the welding surface compared to the cross-section reflects the brief heating time in the sensitization temperature range during welding, resulting in incomplete sensitization through the thickness and thus lower measured reactivation ratios on the cross-section.

Conclusions

1. GBE-processed 304 austenitic stainless steel exhibits excellent 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, the HAZ sensitization zone of GBE-processed specimens demonstrated superior corrosion resistance compared to non-GBE specimens.
3. EPR testing revealed that the sensitization degree of the HAZ sensitization zone in GBE-processed specimens was lower than that of non-GBE specimens for both welding surface and cross-section.

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