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Metallographic screening of grain boundary engineered type 304 austenitic stainless steel

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ABSTRACT

An electrochemical etching method for the identification of grain boundary engineered type 304 austenitic stainless steel microstructures is described. The method can be applied for rapid microstructure screening to complement electron backscatter diffraction analysis. A threshold parameter to identify grain boundary engineered microstructure is proposed, and the application of metallographic etching for characterising the degree of grain boundary engineering discussed.

1. Introduction

Grain boundary engineering (GBE) is now manifested as a potential manufacturing route to design and optimise microstructure for critical application [1]. Typical examples of GBE application include improved intergranular corrosion and stress corrosion cracking resistance, as well as enhanced fatigue and high-temperature creep endurance [2]. Thermo-mechanical process treatments have successfully been explored for the modification of low-to-medium stacking fault energy materials including, for example, austenitic stainless steels [3–5], nickel-base alloys [6], copper and brass [7,8]. Grain boundary network modifications can simply be implemented by changing the relative length or number fraction of low-energy grain boundaries, often described by the Coincidence Site Lattice (CSL) model. The latter describes the inverse volume density of coinciding lattice atom sites at grain boundaries [9]. Interestingly, to avoid bulk material processing, the effect of modifying near-surface microstructures with local GBE treatments has also been explored [10,11].

For extending life-time and resistance towards corrosion-related failures, enhanced material performance is typically associated with significantly increased fractions of $\sum 3$ twin boundaries [4,12,13]. Higher order twins ($\sum 9$ and 27) play an important role for boundary connectivity, breaking up the network of susceptible boundaries [14]; hence forming large clusters of twin-related boundary domains [4,15,16]. The application of electron backscatter diffraction (EBSD) brought about the advent of reliable microstructure analysis, and this technique is now routinely used for texture and grain boundary character distribution (GBCD) analysis. Though sample preparation, data acquisition and data analysis

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require time and are considered as the bottleneck if large throughput production of GBE materials is anticipated.

A metallographic screening procedure for GBE materials is not available, and microstructure GBE modifications are therefore typically characterised by EBSD analysis. The work reported in this paper introduces an electro-chemical microstructure screening method for grain boundary engineered austenitic stainless steels. Microstructure characteristics of thermo-mechanically processed and GBE treated microstructures can be obtained by using a dual-step etching method, with the aim to complement automated EBSD analysis.

2. Material and Methods

A mill annealed, as-received type 304 austenitic stainless steel with a chemical composition of (wt.%) 18.15 Cr, 8.60 Ni, 0.45 Si, 1.38 Mn, 0.055 C, 0.032 P, 0.038 N and 0.005 S was used in this study. GBE microstructures were produced by uni-directionally cold rolling with a reduction of 5% along the mill-rolling direction, followed by an annealing treatment at 950 °C for 24 h. The as-received and GBE materials were polished in the transverse direction to 1/4 micron diamond paste finish, followed by electro-polishing in 92 vol.% acetic acid and 8 vol.% per-chloric acid at 20 °C. EBSD analysis was carried out using a FEI (Philips) XL 30 and FEI Quanta 650 field emission gun scanning electron microscope, both interfaced with Nordlys EBSD detectors. Data acquisition was carried out with HKL Flamenco (FEI XL30) and Oxford Instruments AZtec Version 2.2 software (FEI Quanta 650). EBSD maps with step sizes of 1 and 2 μm over typical areas of 0.5 mm × 0.5 mm and 1 mm × 1 mm were recorded and data processing performed with the in-house software Vmap. Low Angle Grain Boundaries (LAGB) were included with mis-orientations between 1.6° and 15°, and the Brandon criterion was used for CSL boundary analysis [17].

For all electro-chemical tests and metallographic screening, specimens were mounted in an epoxy–resin in the transverse direction, ground with SiC paper and polished with diamond paste to a 1 μm mirror finish. A 42 wt.% nitric acid solution (60:40 ratio – 70 wt.% HNO_3:H_2O) was used for all electro-etching experiments. The electro-chemical behaviour of both microstructures was assessed at room temperature using potentio-dynamic polarisation tests, with the sample acting as working electrode (WE), a platinum sheet as counter electrode (CE) and a saturated calomel electrode (SCE) as reference electrode. To obtain reproducible results, the distance between WE and CE was kept constant at 20 mm, and electro-chemical scans were conducted from +0.1 to +2.5 V relative to the SCE reference electrode by using a scan-rate of 1 mV/s. All obtained data were converted to the standard hydrogen electrode (SHE) scale.

For metallographic screening the same electro-chemical setup was used, with galvano-static polarisation selected for all etching trials. A dual-step etching procedure was applied for microstructure screening. The first etching step was chosen to reveal the general grain boundary network, followed by a second step at a higher current density to reveal lower-energy boundaries within the grain boundary network, such as coherent ∑3 twins. The first step was carried out at a current density of 0.01 A/cm^2 for 120 s. For the second etching step, a larger current density of 1 A/cm^2 was applied for 2 s.

Two coupon samples of the as-received microstructure and two of the GBE conditioned microstructure were assessed, with micrographs after each etching step taken at 200× magnification using a Zeiss Axio LabA1 light optical microscope. Micrographs were recorded at 12 different locations after each etching step, and the number of boundaries counted using a Mean Lineal Intercept (MLI) method on a superimposed orthogonal grid containing 5 × 5 lines. Relatively small areas of approximately 0.5 mm × 0.5 mm were chosen to enable rapid microstructure screening; though larger grids are typically recommended for more robust statistical MLI assessments [18]. The screening method is based on MLI counts of boundaries per unit length after the application of etching step 2, normalised by the MLI counts after etching step 1. This ratio describes the relative difference in boundaries visible after each etching process. All errors represent 95% confidence intervals of the 12 MLI counts.

3. Results & Discussion

The grain boundary character distribution of the as-received and GBE microstructure is summarised in Table 1. The GBE treated microstructure exhibits a higher number of low CSL boundaries, especially ∑3 twins and higher order twins (∑9, 27), whereas the number of LAGBs remained approximately constant. Further information about both microstructures have also been reported elsewhere [4,13].

The potentio-dynamic response of type 304 stainless steel in 42 wt.% nitric acid is summarised in Fig. 1. To assess reproducibility of the results, the as-received and GBE microstructures were tested in triplicates, with the samples re-ground and re-polished between each electro-chemical assessment. Both microstructures showed similar corrosion potentials (E_{corr}) in the range of +0.88 V to +0.84 V vs. SHE. With anodic polarisation both microstructures exhibited passivity up to ≈+1.23 V vs. SHE, followed by a steep rise in current density characteristic of trans-passivity. A similar range of corrosion potentials and electrochemical response was observed in a study of type 304 N austenitic stainless steels in 6 N nitric acid [19].

The chosen etching parameters are indicated in Fig. 1. For etching step 1, the potential difference between corrosion attack at the matrix and grain boundaries is used, as the latter contain excessive energy and are etched preferably [20]. With higher current densities this difference becomes less dominant and most of the attack takes place on grain facets, indicative for step 2. The contouring of the low energy grain

Table 1 – Grain boundary character distribution of the as-received and GBE treated microstructure (number fraction).

	∑1–∑29 [%]	∑3 [%]	∑9, ∑27 [%]	∑1 [%]
As-received	35.2	21.8	3	6
GBE	58.3	35.6	13.1	6.5