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Sensitisation behaviour of grain boundary engineered austenitic stainless steel

Richard Jones, Valerie Randle*

Materials Research Centre, School of Engineering, Swansea University, Singleton Park, Swansea SA2 8PP, Wales, UK

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ABSTRACT

Thermo-mechanical processes involving both single and multiple cycles of low level (5%) strain and annealing were applied to specimens of a type 304 austenitic stainless steel in order to encourage grain boundary engineering (GBE). As a result of the GBE processing the total length proportion of $\Sigma 3^n$ coincidence site lattice (CSL) boundaries was increased from 43% up to a maximum of 75% in conjunction with moderate grain growth. The increases in $\Sigma 3$ and $\Sigma 9$ boundaries resulted in significant decreases in the degree of sensitisation following exposure at 650 °C for up to 4 h and assessment through Double Loop-Electrochemical Potentiokinetic Reactivation (DL-EPR) tests. Over 97% of $\Sigma 3$ boundaries were immune to sensitisation and approximately 80% of $\Sigma 9$ boundaries were either immune or partially resistant to sensitisation, whereas all other CSL boundaries and general boundaries did not resist sensitisation. Therefore, only $\Sigma 3$ and $\Sigma 9$ boundaries were 'special'. Deformation applied by cold rolling was more effective than tensile deformation in bringing about GBE. In summary, the results presented here show that increasing the fraction of $\Sigma 3$ and $\Sigma 9$ boundaries through GBE processing, accompanied by only moderate grain growth, provides an effective route to protection from sensitisation and intergranular corrosion.

1. Introduction

Austenitic stainless steels are used in a wide range of applications due to a combination of good mechanical properties and excellent corrosion resistance across a large temperature range. Corrosion resistance is provided by the formation of a chromium-rich passive layer. In service, when exposed to temperatures between 450 and 900 °C for periods of typically one to hundreds of hours, chromium-rich carbides tend to precipitate at grain boundaries (GBs) [1,2]. Significant carbide precipitation can result in severe chromium depletion near the grain boundary (GB), referred to as sensitisation. Exposure to aggressive environments in a sensitised condition can lead to a breakdown in passivity and consequent intergranular degradation including intergranular corrosion (IGC) and intergranular stress corrosion cracking (IGSCC) [1,3,4]. Sensitised GBs provide connected networks for degradation. Such forms of degradation often limit the service life of austenitic stainless steel components. There are several studies that report measurements of chromium depletion at grain boundaries and attempt to correlate this with microstructure [e.g. 5–8].

The extent and morphology of carbide precipitation and resulting sensitisation have been shown to be dependent on GB structure and energy [8–15]. The field of 'grain boundary engineering' (GBE) has developed over the last two decades aiming to improve intergranular properties in face-centred cubic (fcc) materials through the increase of special GBs imparted during periods of prolific annealing twinning following thermo-mechanical processing [16–18]. GBE has been shown to improve the resistance to sensitisation, IGC, IGSCC, and weld decay in austenitic stainless steels [8–15] The majority of GBE thermo-mechanical processes previously reported on austenitic stainless steels have involved the application of a single-step of processing involving a low level of pre-strain followed by annealing at high temperature for long periods. This report details how GBE processing affects resistance to sensitisation when comparing different processing schedules. These comparisons are use of deformation by cold rolling or tensile testing, single-step versus multiple-step annealing and use of considerably shorter processing times compared to some other work [8–15]. Furthermore, the present work investigates in some detail which particular GB types are sensitisation-resistant. Of course, it should be borne in mind that whereas this paper addresses the link between IGSCC and microstructure, IGSCC is also dependent on the critical interaction between stress, environment and microstructure.

2. Experimental procedure

Thermo-mechanical processing was applied to specimens originating from an as-received (AR) plate of type 304 stainless steel (18.18% Cr, 8.61% Ni, 0.05% C). The plate was supplied following a reduction by cold rolling to 13 mm thickness, mill annealing at 1050 °C and forced air quench. Strain-annealing treatments

* Corresponding author.
E-mail address: v.randle@swansea.ac.uk (V. Randle).

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Table 1
Summary of thermo-mechanical processing applied to as received (AR) type 304 stainless steel.

Microstructure	Starting condition	Strain applied	Annealing conditions	Number of cycles
AR	AR	N/A	N/A	N/A
SA	AR	N/A	2 h @ 1050 °C	1
SSGBE	AR	5% Tensile	30 min @ 1050 °C	1
MSGBE	AR	5% Tensile	30 min @ 1050 °C	3
CRGBE	AR	5% Cold rolled	30 min @ 1050 °C	1
SA/CRGBE	SA	5% Cold rolled	30 min @ 1050 °C	1

consisting of a low level of strain (5%) followed by annealing at 1050 °C were applied in order to produce grain boundary engineered (GBE) microstructures. In order to investigate the role of processing parameters two different pre-strain routes were compared: a uniaxial tensile deformation (5% extension of gauge length) and a 5% reduction in thickness by cold rolling. Following the application of the 5% pre-strain, specimens were annealed at 1050 °C in air for 30 min and water quenched. To investigate the role of multiple processing cycles compared with single-step processing, 3 complete cycles of 5% tensile deformation followed by annealing were carried out. A solution annealing (SA) treatment consisting of a 2-h treatment at 1050 °C provided an alternative starting condition for a single-step strain-annealing process using the cold rolling deformation path. All thermo-mechanical treatments and resulting microstructures are summarised in Table 1. The specimens are referred to as single-step GBE (SSGBE), multiple-step GBE (MSGBE) and cold rolled GBE (CRGBE).

Following thermo-mechanical processing all specimens were prepared using standard metallographic procedures for electron backscatter diffraction (EBSD) analysis. Colloidal silica polishing and etching in 10% oxalic acid at 6 V comprised the final stages of specimen preparation. EBSD orientation mapping by Channel 5 software from HKL Technology was performed in a Philips XL30 scanning electron microscope (SEM) was used to collect microstructure and misorientation data from all specimens. Length proportions of $\Sigma3^n$ ($n \leq 3$) and other CSL boundaries were automatically calculated with boundaries being categorised according to the Brandon criterion [19]. In orientation maps GBs with misorientations ranging 5–15° were characterised as low angle GBs and all non $\Sigma3^n$ boundaries with misorientation above 15° were characterised as random high angle GBs. Grain sizes pre- and post-processing were assessed using automated mean linear intercept (MLI) measurements. $\Sigma3$ Boundaries were counted as grain boundaries.

All specimens (excluding SA) were subjected to thermal heat treatments in order to encourage the precipitation of carbides at GBs and hence to encourage sensitisation. Specimens measuring 6 mm × 6 mm × 1.5 mm were subjected to heat treatment at 650 °C in air for 1 and 4 h and air cooled. Previous work using the same as-received material had shown that a 1-h treatment resulted in ≈22% degree of sensitisation (DOS) and a 4-h treatment resulted in a ≈77% DOS [20], where 'degree of sensitisation' refers to what proportion of boundary length has been sensitised. The present work has used the same experimental conditions in order to aid comparison with the previous work. All microstructures (excluding SA) were assessed for sensitisation propensity via Double Loop-Electrochemical Potentiokinetic Reactivation (DL-EPR) tests. A testing procedure similar to that stipulated in British Standard BS ISO 12732:2006 [21] was applied using a 0.5 M H_2SO_4 + 0.01 M KSCN solution. A scan rate of 2160 mV/h was used under the control of a Versastat potentiostat and Corrware software. DOS was assessed according to the ratio I_r/I_p, of the two peak currents during the cathodic reactive (I_r) and anodic polarisation (I_p) scans. Three scans were performed on each specimen.

The misorientation of GBs resistant or susceptible to sensitisation was assessed post DL-EPR testing by using combined SEM and EBSD analysis. Backscattered and secondary electron micrographs and EBSD orientation maps of the same area were collected from each specimen. Etching at GBs revealed boundaries attacked during DL-EPR testing, whereas non-etched boundaries were resistant to corrosion by etching. Comparison with corresponding orientation maps revealed the nature of the GBs resistant or susceptible to sensitisation.

3. Results

3.1. GB misorientations

Application of thermo-mechanical GBE processing to the type 304 stainless steel specimens had increased the length proportions of $\Sigma3^n$ ($n \leq 3$) CSL boundaries as indicated in Fig. 1. These statistics offer a first order indication of GBE success as they are indicative of GBE mechanisms occurring involving $\Sigma3$–$\Sigma3$ interactions via the '$\Sigma3$ regeneration mechanism' [18]. Briefly, after prolific annealing twinning an encounter between two $\Sigma3$ boundaries will result in the generation of a $\Sigma9$ boundary. If this boundary subsequently encounters a new $\Sigma3$ boundary, another $\Sigma3$ boundary will be generated to complete the new triple junction. Furthermore $\Sigma3^n$ boundaries are often attributed 'special' status and also they tend to disrupt the connectivity of random GB pathways. A complete breakdown of $\Sigma3^n$ ($n \leq 3$) boundary length fractions for each specimen is presented in Table 2.

A single-step of 5% tensile deformation followed by annealing at 1050 °C (SSGBE) resulted in moderate increases in $\Sigma3^n$ boundaries compared to those found in the AR type 304 stainless steel. The length fraction of $\Sigma3$ boundaries was noticeably increased from 40.5% in the AR condition to 53.2% following SSGBE processing. Higher order twin boundaries ($\Sigma9$ and $\Sigma27$) were only modestly increased (Fig. 1, Table 2). Repetition of this treatment for three complete cycles (MSGBE) resulted in further increases in $\Sigma3^n$ boundary length proportions with higher order twin boundaries being more noticeably increased (Fig. 1, Table 2). Multiple-step processing involving a low level of tensile deformation was there-

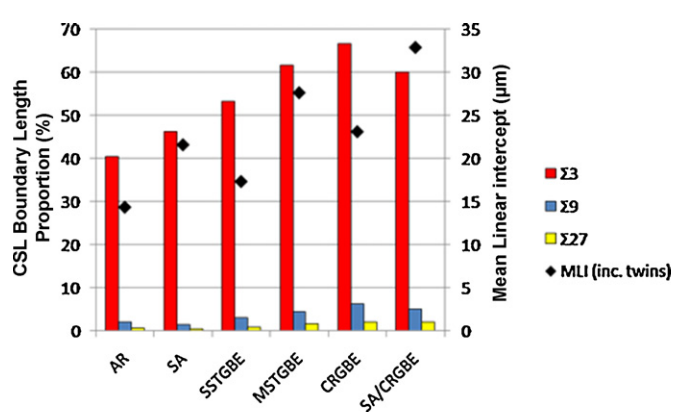

Fig. 1. Changes to $\Sigma3^n$ boundary length proportions and mean linear intercept grain sizes (including twin boundaries) with thermo-mechanical processing of type 304 stainless steel.