Grain boundary engineering for crack bridging:
a new model for intergranular stress corrosion crack
(IGSCC) propagation

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Abstract

The first in-situ high-resolution X-ray tomography of stress corrosion cracking in a fully
sensitised austenitic stainless steel indicates the build up of un-fractured ligaments within the
cracking path. This is attributed to corrosion resistant grain boundaries and their associated triple
junction (TJ) fractions. A simple grain bridging model has been introduced to quantify the effect
of static stress and crack bridging on crack length development. Grain boundary engineering, by
thermomechanical treatments, has been used to modify microstructural features, such as grain
size, grain boundary character and TJ density distributions, studied using electron backscatter
diffraction. A progressive shift to higher “special” TJ compositions, in form of participating low
energy grain boundaries, is achieved. The new model successfully predicts the effect of grain
boundary engineering on the maximum crack length.

1. Introduction

The idea of “Grain Boundary Design” [1] in polycrystalline materials has been
investigated for more then two decades. The goal of changing intergranular properties
in low and medium stacking fault energy f.c.c. materials is reflected by a vast and
steadily growing variety of scientific literature, comprising investigations to classify a
broad range of microstructures [2–5], their microstructural evolution [6–8] and related
mechanisms [9–11] as well as associated properties [12–14]. A large part of this
research is directed at improving the intergranular corrosion (IGC) (e.g. Refs. [15,16])
and intergranular stress corrosion cracking (IGSCC) resistance (e.g. Refs. [17,18]).

Bulk property enhancements are generally associated with improvements in the
overall population of beneficial low energy grain boundaries. However, it is apparent
that other factors might have significant effects, such as triple junction (TJ) populations
[19], spatial grain boundary (GB) network connectivity considerations [20,21], as well
as geometric effects which are able to influence possible susceptibility criteria, such as the deviation of GBs from exact fit [22] or GB-plane influences [18,23].

The coincidence site lattice (CSL) model, which categorizes the crystallographic relation of two adjacent point lattices, is conveniently applied [24]. Common sublattices of both crystals are used to describe the GB type. The Σ-designation describes the inverse volume density of coinciding atom sites (CSL model) at the interphase. This geometrical framework has gained widespread attention, since it is an easily applied evaluation procedure, included in commercially available software. However, care has to be taken in which boundary statistics are extracted (relative length or frequency) [25,26] and in particular, regarding applications, which GB types are considered to possess “special” properties.

In-situ high-resolution tomography observations have led to a new approach to understand the influence of microstructure on IGSCC. It is proposed that the crack is only locally arrested at a TJ (as seen in a 2D section), and can propagate around the barrier due to its 3D nature. This leaves a non-fractured GB as bridging ligament. A simple crack-bridging model has been developed, which considers the shielding effect of these ligaments on the crack tip stress intensity factor. This paper summarizes significant high-resolution X-ray tomography results, followed by the introduction of a new IGSCC propagation approach and concludes with a description of the microstructural evolution and classification of selected microstructures to evaluate the model.

2. Experimental procedure

Two austenitic stainless steels have been used in this study (Table 1). The high resolution X-ray tomography investigation was carried out by using Type 302 wire specimens with a diameter of approximately 0.4 mm, which were cut in small sections of 30 mm length. Microstructural evolution and related model evaluation experiments (IGSCC) were studied with Type 304 plate material which was cut into oblong shaped bars with dimensions of 150 mm × 20 mm × 13 mm (L × W × T).

<table>
<thead>
<tr>
<th>Type</th>
<th>Shape</th>
<th>Fe</th>
<th>Cr</th>
<th>Ni</th>
<th>C</th>
<th>Mn</th>
<th>P</th>
<th>S</th>
<th>Si</th>
<th>N</th>
<th>Condition</th>
</tr>
</thead>
<tbody>
<tr>
<td>302</td>
<td>Wire</td>
<td>Bal.</td>
<td>18.14</td>
<td>8.60</td>
<td>0.070</td>
<td>1.25</td>
<td>0.025</td>
<td>0.003</td>
<td>0.40</td>
<td>n.a.</td>
<td>Cold drawn</td>
</tr>
<tr>
<td>304</td>
<td>Plate</td>
<td>Bal.</td>
<td>18.15</td>
<td>8.60</td>
<td>0.055</td>
<td>1.38</td>
<td>0.032</td>
<td>0.005</td>
<td>0.45</td>
<td>0.038</td>
<td>Annealed</td>
</tr>
</tbody>
</table>

2.1. High-resolution X-ray tomography/Grain bridging

In-situ observations of IGSCC have been performed using high resolution X-ray tomography at the European Synchrotron Radiation Facility. These observations allowed the crack to be observed in 3D within the test specimen. The initiation of cracking and specimen failure due to crack coalescence was recorded.

The Type 302 wire was solution annealed at 1050°C for 30 min and then exposed at 650°C for 60 min, producing a fully sensitised microstructure. All heat treatments were carried out in argon atmosphere with a subsequent water quench. IGSCC experiments
were performed in a 0.15 mol tetrathionate solution (K₂S₄O₆), acidified with diluted sulphuric acid (H₂SO₄) to pH 2. The electrochemical set-up, experimental procedure and information about the high resolution X-ray tomography experiments are described elsewhere [27,28].

2.2. Microstructural evolution and classification

Thermomechanical treatments of the pre-cut Type 304 bars, in form of cold rolling followed by heat treatments, were used to prepare a variety of different microstructures (Table 2). All cold reduced bars were cut with a precision saw perpendicular to the rolling direction before carrying out the thermal treatments, to produce small, parallel sided specimens for scanning electron microscopy (SEM) and electron backscatter diffraction (EBSD) analysis. Individual heat treatments were carried out in argon atmosphere, followed by a water quench. One surface was ground and polished with diamond paste to a 1/4 µm finish. A subsequent electro-polish in 92 vol.% acetic acid and 8 vol.% perchloric acid, by applying 45 V direct current for 30 to 60 s, provided a strain-free surface condition.

Table 2
Thermomechanical treatment conditions to classify microstructural evolution processes

<table>
<thead>
<tr>
<th>Process type</th>
<th>Cold reduction (%)</th>
<th>Heat treatment (°C)</th>
<th>Exposure time (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Single reduction</td>
<td>30</td>
<td>900</td>
<td>2-60</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>1050</td>
<td>2-60</td>
</tr>
</tbody>
</table>

The microstructures were studied with a HKL-EBSD system, interfaced to a Philips XL-30 FEG-SEM. Three to five grids with minimum 500 µm × 500 µm and up to 750 µm × 750 µm, by using a step size of 5 µm, were analysed on each sample. The grid and step size were chosen to identify microstructural tendencies, rather then precise grain boundary or TJ populations, since short GB segments (e.g. <5 µm) are not necessarily sampled. However, by drawing “worst case” analogies to grain or sub-grain size measurements [29,30], relatively small errors are expected.

An in-house developed software package (Vmap) was used to extract information about GB character (GBC) and TJ density (TJD) distributions, using CSL model. Brandon’s criterion (Δθ = 15Σ⁻¹/₂) [31] was applied for the maximum allowable deviation angle. A data cleaning procedure, by assigning the orientation of the neighbour closest pixel to the neighbour average (of at least 2 adjacent pixels) to non-indexed points, was performed [30]. Low CSL GBs were identified up to Σ29 and include low angle grain boundaries (LAGB). The misorientation range between 1.6 and 15° was used as LAGB criterion. Grain sizes, including the counting of coherent twin GBs, were also extracted from the EBSD data. Averaged mean values were used to describe the microstructures. The range of minimum and maximum mean populations provide an indication of measurement uncertainties (Table 3).

In this study, only GB frequencies [3,30] and their related TJDs are reported. An algorithm for comparing adjacent pixels around 2 different pixel orientations (GB region) was employed to get information about apparent TJs and their participating GB types (Vmap). TJs were then evaluated semi-qualitatively, by categorizing them into
Table 3
Thermomechanical treatment conditions of specimen produced for further IGSCC tests

<table>
<thead>
<tr>
<th>Sample</th>
<th>Thermomechanical treatment</th>
<th>Sensitisation time / temp.</th>
<th>Grain size (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Av. mean</td>
</tr>
<tr>
<td>900/30</td>
<td>30% reduction / 900°C for 30 min</td>
<td>24 h / 650°C</td>
<td>10</td>
</tr>
<tr>
<td>1050/10</td>
<td>30% reduction / 1050°C for 10 min</td>
<td>24 h / 650°C</td>
<td>19</td>
</tr>
</tbody>
</table>

classes of participating low CSL GBs (e.g. 0-, 1-, 2- or 3-CSL TJ), to determine the relative fraction of each type.

2.3. IGSCC experiments

Two microstructures (Table 3) were selected for IGSCC experiments. All heat treatments were carried out in argon atmosphere with a subsequent water quench. The degree of sensitization was qualitatively confirmed by using ASTM A262 (practice A). Double-beam bend (DBB) specimen with a thickness of 1.5 mm were produced, loaded to 200 MPa according to ASTM G39 and exposed to a 0.1 mol K$_2$S$_2$O$_8$ solution, acidified to pH 2.5 (with diluted H$_2$SO$_4$) for 144 h. Preliminary experiments established suitable conditions for IGC and IGSCC tests. Following exposure, all DBB specimens were cut along the spacer contact points, and bent for 90° over a radius of 3 mm to open existing cracks. The longest crack of at least 3 examined sections, situated along and parallel to the middle fibre, was recorded. The application of extreme value statistics is anticipated for further analysis [32,33].

3. Results

3.1. High-resolution X-ray tomography / grain bridging

High-resolution X-ray tomography has been demonstrated as a tool for observing intergranular corrosion and cracking [27,28]. Computer reconstructed volumes of the exposed region show the propagating crack. Analysis of 2D sections of the data implies that the crack is discontinuous (Fig. 1a). However, 3D visualisation of the same region, by reconstructing the crack surface, show that the crack is, in fact, continuous (Fig. 1b), but is bridged by un-fractured ligaments.

The intergranular crack path shows small ductile regions (Fig. 2). The morphology of these regions is consistent with twin related low energy boundaries. More detailed observations of reconstructed bridging regions with subsequent failures, resulting in broken ligaments, are reported elsewhere [27,28]. A 2D image of an intergranular crack, in conjunction with a schematic diagram explains the build up of the bridges (Fig. 3).

3.2. The new IGSCC propagation model

IGSCC prediction models based on “special” GB or TJ statistics were introduced in the early 1990s [34]. A stochastic model (Eq. (1)) considers the frequency of immune GBs ($\Sigma \leq 29$) with respect to the microstructural probability ($P$) of arresting a crack at a TJ
Fig. 1. Reconstructed section of the observed intergranular cracking with: (a) discontinuous 2D section of the crack path; and (b) 3D iso-crack surface reconstruction of the same region. The crack in (b) is rendered opaque and the material transparent.

Fig. 2. Post-mortem fracture analysis showing regions that failed in a ductile manner.

Fig. 3. 2D section of an intergranular crack, highlighting some “unbroken sections” with a sketch, explaining the bridge build up resulting in ductile ligaments.
This is reflected in the maximum critical crack length \((L)\), and influencing factors such as grain size \((d)\) and total probability of crack arrest \((\chi)\).

\[
(1 - \chi) = (1 - P)^{2L/d}
\]

Further developments of this model are mainly achieved through modifying GB- or TJ-immunity conditions, by discounting “neutral twins” [35] or considering exclusively \(\Sigma 3\)-containing TJs [36] for the microstructural probability \((P)\).

Alternative approaches include percolation theory based models, consisting of analytically determined threshold borders for selective GB attack through sensitisation [37], Cr depletion [38], TJ susceptibilities [39] or the introduction of “special GB” cluster morphologies with quantitative GB-network assessments [40]. Several numerical models, based on a variety of approaches show the widespread development in this area (e.g. Refs. [41,42]). However, the majority of these models do not consider any mechanical driving force for crack propagation, which is essential if, for example, the effect of residual stress are to be modelled.

The observation of grain bridging has suggested a new approach of predicting intergranular stress corrosion crack length distributions. The key premise of this model is that bridges arise from the local arrest at “cul-de-sac” \((2\text{-CSL TJ})\) or unfavourably orientated triple junctions \((1\text{-CSL TJ})\). The bridge is formed by 3D propagation around the TJ, leaving the non-fractured boundary as a bridge (Figs. 1 and 2). This causes a bridging stress in the wake of the crack tip, which leads to crack tip shielding. The rate at which crack tip shielding develops controls the maximum crack length, and the threshold stress for stress corrosion cracking \((SCC)\) resistance.

The tendency for bridge formation is described by the microstructure resistance factor \((P)\), which depends on the fraction of TJs that are potentially able to arrest the crack. This is expressed by Eq. (2):

\[
P = \left( f_a f_{(2\text{-CSL TJ})} + f_b f_{(1\text{-CSL TJ})} \right) / \left( 1 - f_{(3\text{-CSL TJ})} \right)
\]

The fractions of 2-CSL \((f_{(2\text{-CSL TJ})})\) and 1-CSL TJ \((f_{(1\text{-CSL TJ})})\) are considered to be beneficial whereas the 3-CSL TJ \((f_{(3\text{-CSL TJ})})\) are subtracted from the overall population, since they cannot be reached by the crack. All low CSL GBs \((\Sigma \leq 29)\) are currently assumed to be crack resistant, although this could be modified to include other definitions of GB or TJ immunity depending on material and environment. The geometrical factors \((f_a, f_b)\) are dependent on the microstructure (e.g. grain shape) and are assumed to be \(f_a = 1\) and \(f_b = 0.5\). This accounts for a complete arrest at 2-CSL TJ and a partial \((50\%)\) arrest at “unfavourably orientated” 1-CSL TJ. In its current form, the model does not consider the probability of influencing the crack at 0-CSL TJs.

Crack arrest by a single junction is not expected to significantly affect the behaviour of a crack with a size greater than several grains. However, the cumulative effect of grain bridging gives rise to a shielding stress, which reduces the stress intensity factor at the crack tip. Several microstructure dependent factors lead to the shielding stress. Firstly, the number of bridges per unit area is assumed to vary in proportion to the resistance factor. Secondly, the bridge size, and thus its contribution to the shielding stress, depends on the grain size, which is related to the spacing of effective TJs. Finally, the degree of shielding is assumed to build up and then saturate at steady state with increasing crack length. This is due to the reduced probability of encountering
resistant boundaries along the curved crack front when the crack length is short compared to the triple junction spacing. The bridge strength is assumed to be approximated by the tensile strength ($\sigma_{UTS}$).

The crack length for steady state ($a_{sat}$) is not known, but a reasonable assumption would be of the order of 10 grain diameters (d, including twin GBs). The average bridging stress ($\sigma_{br}$) therefore depends on the crack length (a), the microstructure resistance factor ($P$), the ultimate tensile strength ($\sigma_{UTS}$) and the crack length at which the shielding stress reaches steady state ($a_{sat}$). The saturation factor ($f$) increases linearly from 0 to 1 as the ratio of crack length (a), to the maximum saturation length ($a_{sat} = 10d$) reaches its maximum shielding capability (Eq. (3)).

$$\sigma_{br} = f P \sigma_{UTS}$$

$$f = a / a_{sat} \text{ for } a < a_{sat}$$

$$f = 1 \text{ for } a \geq a_{sat}$$

The shielding effect of the bridging stress is estimated by assuming that the stress acts over the entire crack length. Linear elastic fracture mechanics (LEFM) is currently assumed, which is reasonable at low stresses. The shielding stress intensity ($K_{sh}$) due to an average bridging stress ($\sigma_{br}$) over the area of a semi-circular crack with depth (a), is estimated as follows:

$$K_{sh} = \sigma_{br} \sqrt{(a / 2\pi)}$$

A threshold stress ($\sigma_{th}$) for crack propagation can be calculated, given a value for the local threshold stress intensity factor ($K_{SICC}$). The critical threshold stress is the maximum stress above which cracks do not arrest. Below this value, cracks may nucleate, but arrest due to the rising resistance to crack propagation.

$$\sigma_{th} = \sqrt{2\pi (K_{sh} + K_{SICC}) / a}$$

The degree of crack tip shielding afforded by this bridging mechanism is quite small, and there is therefore only a significant effect on the threshold stress for crack propagation if the intrinsic value for $K_{SICC}$ is small (e.g. 0.1 MPa√m). This is consistent with observations of very small crack tip opening displacements for IGSCC [43] and implies that stress corrosion crack propagation effectively requires sufficient crack tip deformation to strain the crack tip. The model is not sensitive to the particular value of $K_{SICC}$ in this range.

3.3. Microstructural evolution and classification / IGSCC experiments

The microstructural developments of grain size, low CSL GB frequency (F CSL) and TJD distributions, with respect of increasing exposure periods, are shown in Figs. 4 and 5. Low temperature (900°C) annealing treatments resulted in a stable grain size with a slight increase of low CSL GB frequencies. The short term (2 min / 900°C) exposure does not appear to be fully recrystallized, which was reflected in a very high LAGB fraction (∼20%). A general exposure time dependent trend of decreasing 0-CSL TJs, with slightly increasing 1-CSL and 2-CSL TJs was found. 3-CSL TJs appeared to
be not affected significantly by these processing conditions. The 1050°C annealing treatment showed more distinctive features, in the form of grain size and special GB-fraction growth. A TJD shift from 0-CSL to 1-, 2- and 3-CSL TJ's is more apparent.

A comparison between a stochastic model [34], a recent enhancement of this model [35] and the grain bridging approach provide insight in the range of maximum predicted crack lengths of the selected structures (Table 4). $K_{SCC}$ was taken as 0.1 MPa√m and the ultimate tensile strength of an annealed austenitic stainless steel as 600 MPa. Calculated probability factors (P) are based on the microstructural evolution study, with $f_0 = 1/3$ [34] and, for the purpose of adequate comparisons, all used grain sizes include twin boundaries. Calculated crack length ratios of both microstructures provide an indication of the ranking (Table 4). The bridging model predicts crack lengths that vary approximately linear for stresses below the threshold stress ($\sigma_{th}$).
Table 4
Comparison of determined probability factors (P) with predicted and measured critical crack lengths and their corresponding crack length ratios

<table>
<thead>
<tr>
<th>Model</th>
<th>900/30 (P)</th>
<th>1050/10 (P)</th>
<th>Probability (χ)</th>
<th>900/30 (L₁) [µm]</th>
<th>1050/10 (L₂) [µm]</th>
<th>Ratio (L₁/L₂)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stochastic model [34]</td>
<td>0.20</td>
<td>0.22</td>
<td>99.9%</td>
<td>150</td>
<td>270</td>
<td>0.55</td>
</tr>
<tr>
<td>Stochastic Enhancement</td>
<td>0.29</td>
<td>0.17</td>
<td>99.9%</td>
<td>70</td>
<td>350</td>
<td>0.20</td>
</tr>
<tr>
<td>Bridging model</td>
<td>0.34</td>
<td>0.37</td>
<td>at 200 MPa</td>
<td>80</td>
<td>160</td>
<td>0.50</td>
</tr>
<tr>
<td>Measured after IGSCC test</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>460</td>
<td>800</td>
<td>0.58</td>
</tr>
</tbody>
</table>

4. Discussion

The build up of ductile bridging ligaments is assumed to be linked to less susceptible GBs, with a distribution controlled by the TJD. The grain boundary characters of the bridged regions are currently under investigation. A variety of related factors might account for these system dependent immunity behaviours, including GB-sensitisation susceptibilities [44–46], corresponding Cr-depletion levels [38,44], or other influences such as environment [47], geometrical [18] or GB structure dependent behaviour [13,47].

Microstructural evolution, in form of significantly increased low CSL fractions, to improve the general corrosion or cracking resistance, can be achieved by either iterative multi-step treatments with short annealing periods [7,48], a single low reduction process with prolonged low temperature anneals [16], or a medium reduction followed by a very short annealing period [10]. These processes are designed to avoid any appreciable grain growth [9,48], mainly for the sake of mechanical property requirements. However, even ordinary thermomechanical processing conditions shift network topologies. Analytical and simulated probability studies [5], relating “special” GB frequencies to triple junction density evolutions indicate microstructural development trends. The apparent tendency of increasing 1-CSL TJ fractions (Figs. 4 and 5), which is related to the relatively low “special” GB frequencies (e.g. < ~1/3) [5,49], results in a primary shift of 0-CSL to 1-CSL TJ populations. Increasing the fraction of low CSL GBs (e.g. > ~1/3), with regard of the main constituent (twins), provides multiple twin interactions, producing mainly 2-CSL and 3-CSL TJs [38,40,49], with a reduction of 1-CSL TJ fractions [40].

Low temperature anneals keep grain sizes small, but result in relatively small changes of GBC and TJD distributions (Fig. 4). Prolonged exposure times are needed to compensate this relation [16]. The observed increase of special GB frequency of the 1050°C annealing treatment is possibly linked to grain growth processes [50]. The influence of conventional thermomechanical processes on the grain boundary character shows that the thermomechanical processing history may have an important effect of the microstructural condition in IGSCC.

The new 2D approach is a simplified representation of the crack behaviour, and acts as a test for the significance of the observed crack bridging ligaments. In its current form, the model can be used to rank the resistance of microstructures in terms of maximum expected crack length under a constant static stress, and the static stress threshold for unstable crack propagation. Measured maximum crack lengths followed the predicted tendency, which is supported by the ratios between prediction and
measurement (Table 4). The new model, which is consistent with mechanistic observations, gives similar rankings to the principal stochastic models and appears to be reasonable. The principal aim of the model is to provide a tool for predicting the effects of residual stresses on the behaviour of IGC and SCC. This is the first attempt to quantify the effect of grain bridging as an influencing factor in IGSCC. Experiments to correlate applied stress levels with their predicted crack length distributions are currently under investigation and should lead to a further refinement of the model.

5. Conclusion

A new IGSCC propagation model is introduced based on grain bridging by crack resistant, low energy GB and their related TJDs. Preliminary tests showed the feasibility of this model, by ranking the microstructure according to their expected cracking distances. Grain boundary engineering can be used as a tool to create a variety of different microstructures for the purpose of model evaluations.

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References


