Application of Grain Boundary Engineering to Improve Resistance of Alloy 625 Plus to Hydrogen Embrittlement

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For

Mom, Dad, Aaron, Sam, and Bill
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# Table of Contents

List of Figures .................................................................................................................. v

Abstract ............................................................................................................................... x

Chapter 1: Motivation and Aims ....................................................................................... 1
  1.1: Motivation .................................................................................................................. 1
  1.2: Aims .......................................................................................................................... 2

Chapter 2: Background and Literature Review ............................................................... 3
  2.1: Grain Boundaries ....................................................................................................... 3
    2.1.1: Grain Boundary Characteristics ......................................................................... 3
    2.1.2: The Coincident Site Lattice Model .................................................................... 4
  2.2: Recrystallization ......................................................................................................... 6
  2.3: Twin Formation .......................................................................................................... 9
  2.4: Grain Boundary Engineering ..................................................................................... 12
    2.4.1: Grain Boundary Engineering Methods ............................................................... 12
    2.4.2: Evaluating GBE Microstructures ..................................................................... 14
    2.4.3: Twin Related Domains ..................................................................................... 15
  2.5: Nickel Superalloys ..................................................................................................... 19
  2.6: Hydrogen Embrittlement ............................................................................................. 21
    2.6.1: Decohesion .......................................................................................................... 22
    2.6.2: Hydrogen Enhanced Localized Plasticity ............................................................. 22

Chapter 3: Experimental Methods ................................................................................... 27
  3.1: Alloy Selection .......................................................................................................... 27
  3.2: Surface Study ............................................................................................................. 29
    3.2.1: Sample Conditions ............................................................................................. 29
    3.2.2 EBSD Analysis ..................................................................................................... 30
  3.3: Iterative Processing ..................................................................................................... 31
  3.4: TRD Size Estimation .................................................................................................. 32
  3.5: RSL Testing ................................................................................................................ 33
  3.6: Post RSL Fractography and Strain Analysis ............................................................... 34

Chapter 4: Results .............................................................................................................. 36
  4.1: Surface Study ............................................................................................................. 36
  4.2: Iterative Study ............................................................................................................ 40
  4.3: TRD Size Measurement .............................................................................................. 44
List of Figures

Figure 1: A schematic of a \(\Sigma 5\) relationship between two simple cubic lattices, where the two lattices are superimposed and coincident sites are shown as black dots [1].................. 4

Figure 2: Plots of grain boundary energy vs. misorientation angle in Al and Cu [2]........ 5

Figure 3: a) A schematic of a coherent twin boundary. b) A schematic of an incoherent twin boundary [3]........................................................................................................... 6

Figure 4: A kernel average misorientation map of a partially recrystallized sample of alloy 625 plus, where recrystallization was initiated by SIBM after a 5% rolling reduction and 2 hour anneal at 925°C. Grain boundaries overlaid with RHAGBs in black, \(\Sigma 3\) in red, \(\Sigma 9\) in green and \(\Sigma 27\) in blue. .............................................................. 9

Figure 5: A schematic showing the formation of annealing twins via the growth-accident model [10].......................................................................................................................... 10

Figure 6: Summary of processing conditions and resulting CSL length fraction in 317L stainless steel. Samples are labelled as rolling reduction-annealing temp-annealing time [21]........................................................................................................ 14

Figure 7: A TRD tree diagram adapted from [22]. .................................................................................. 16

Figure 8: a,b) Example TRDs, with a being simple and b being more complex. c,d) Tree diagrams for the TRDs shown in a and b. e,f) Experimental examples of simple and complex TRDs in stainless steel [21]........................................................................................................ 17

Figure 9: Schematic showing the formation of a TRD with the twin relationship tree inlaid [23]......................................................................................................................... 18

Figure 10: Summary of GBE processing conditions and resulting grain size and TRD size. Samples are labelled as rolling reduction-annealing temp-annealing time [21]...... 19

Figure 11: Cuboidal \(\gamma'\) precipitates protruding from a fracture surface. ......................... 20

Figure 12: a) Slip traces and b) dimples on intergranular fracture surfaces, evidence of dislocation interactions at the fracture surface. Adapted from [33] and [34]. ................. 23

Figure 13: A plot of shear stress on a dislocation as function of distance from another location at varying levels of hydrogen charging [32]. ......................................................... 24
Figure 14: Dislocation cell structures at a hydrogen embrittled fracture surface in Ni-201 [33]

Figure 15: A phase diagram, produced in JMatPro with intermetallic phases restricted to $\gamma'$ and $\gamma''$, courtesy of Carpenter Technologies.

Figure 16: TTT diagram for 625 plus produced using JMatPro, courtesy of Carpenter Technologies.

Figure 17: A schematic showing how samples were cut from iteratively processed bars.

Figure 18: Kernel average misorientation maps for the 5R_L and 5R_H conditions with grain boundaries overlaid with RHAGBs in black, $\Sigma 3$ in red, $\Sigma 9$ in green and $\Sigma 27$ in blue. A) 5R_L shows no evidence of recrystallization. B) 5R_M shows only partial recrystallization.

Figure 19: Unique grain color maps ignoring CSL boundaries with RHAGBs overlaid in black, $\Sigma 3$s in red, $\Sigma 9$s in green, and $\Sigma 27$s in blue. This type of map will herein be referred to as a TRD map. A) SA B) 5R_H C) 10R_M D) 25R_M

Figure 20: Bar graph of the percentage of each type of triple junction (0/1, 2, or 3 CSL boundaries).

Figure 21: Graphs showing the evolution of CSL length fraction and interconnectivity with each iteration of processing.

Figure 22: Summary of the grain size measured at the surface center and in cross section for three iterations of the 5R_H and 10R_M processes.

Figure 23: TRD map of a 5R_H_3 sample after a double aging treatment.

Figure 24: TRD map of the nine EBSD scans stitched together from the SA sample.

Figure 25: TRD maps of the nine scans used to estimate TRD size of the final GBE condition.

Figure 26: TRD size distributions for the GBE sample by number and area.

Figure 27: A) An RSL fracture surface tested in air with regions 1, 2, and 3 corresponding to the notch, pre-crack, and ductile failure region with the crack propagation upwards. B) An RSL fracture surface tested in hydrogen charging conditions with regions 1, 2, 3, and 4 corresponding to the notch, pre-crack, subcritical crack growth, and ductile failure region with the crack propagating to the right.
Figure 28: SEM micrograph of a pre-cracked region. .......................................................... 49

Figure 29: SEM micrograph of a ductile, final failure region, with gamma prime precipitates protruding from the surface. ................................................................. 49

Figure 30: SEM micrograph of the subcritical crack growth region of the SA sample tested in hydrogen. ........................................................................................................... 50

Figure 31: SEM micrograph of the subcritical crack growth region of the 5R sample tested in hydrogen. ........................................................................................................... 51

Figure 32: SEM micrograph of the subcritical crack growth region of the 10R sample tested in hydrogen. ........................................................................................................... 51

Figure 33: Dislocation density map of the SA air sample cross section with color scale shown in Log_{10} of the dislocation density and x and y axis labels in hundreds of μm’s. Boundaries overlaid with RHAGBs in black, Σ3s in red, Σ9s in green, and Σ27s in blue. ......................................................................................................................... 52

Figure 34: Dislocation density map of the GBE air sample cross section with color scale shown in Log_{10} of the dislocation density and x and y axis labels in hundreds of μm’s. Boundaries overlaid with RHAGBs in black, Σ3s in red, Σ9s in green, and Σ27s in blue. ......................................................................................................................... 52

Figure 35: SEM micrograph of the cross section of the SA hydrogen charged sample where EBSD was performed. ......................................................................................................................... 53

Figure 36: Dislocation density map of the SA hydrogen charged cross section with color scale shown in Log_{10} of the dislocation density and x and y axis labels in hundreds of μm’s. Boundaries overlaid with RHAGBs in black, Σ3s in red, Σ9s in green, and Σ27s in blue. Arrows indicate regions of low plastic strain at the fracture surface.............................. 54

Figure 37: SEM micrograph of the cross section of the 5R hydrogen charged sample where EBSD was performed. ......................................................................................................................... 54

Figure 38: Dislocation density map of the 5R hydrogen charged cross section with color scale shown in Log_{10} of the dislocation density and x and y axis labels in hundreds of μm’s. Boundaries overlaid with RHAGBs in black, Σ3s in red, Σ9s in green, and Σ27s in blue........................................................................................................................................ 55

Figure 39: A list of Σ3 boundaries for n=1 to 6 [44]. ..................................................................... 58
Figure 40: Intergranular fracture surface facets from an SA sample with arrows pointing to slip traces. ................................................................. 61

Figure 41: Intergranular fracture surface facets from an 5R sample with arrows pointing to slip traces. ............................................................. 62

Figure 42: Dislocation density map of the 5R hydrogen charged cross section with color scale shown in Log$_{10}$ of the dislocation density and x and y axis labels in hundreds of μm’s. Boundaries overlaid with RHAGBs in black, Σ3s in red, Σ9s in green, and Σ27s in blue. Arrows indicate areas where dislocations are localized around twin boundaries or into subgrain structures. ................................................................................. 63
List of Tables

Table 1: Nominal composition of alloy 625 plus [43] .................................................. 27
Table 2: Sample conditions .................................................................................................. 29
Table 3: Results of GBE surface study .................................................................................. 36
Table 4: Threshold stress intensity values from RSL testing ................................................. 47
Table 5: Summary of microstructure and RSL test results .................................................. 59
Abstract

Application of Grain Boundary Engineering to Improve Resistance of Alloy 625 Plus to Hydrogen Embrittlement

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The field of grain boundary engineering seeks to improve various materials properties by promoting the formation of low-energy grain boundaries such as the coherent Σ3, or twin, boundary. This field has historically relied on empirically discovered methods with little understanding of the underlying mechanisms. More recently it has come to light that the primary mechanism for the development of grain boundary engineered microstructures is the growth of large twin related grain clusters known as TRDs.

One property that grain boundary engineering may be applied to is improving resistance to hydrogen embrittlement. Hydrogen embrittlement is a deterioration of mechanical properties in a metal exposed to hydrogen, characterized by brittle, intergranular fracture at low applied stresses. While grain boundary engineering has been applied to mitigate this issue, ambiguity in the mechanisms behind hydrogen embrittlement leads to ambiguity in the mechanism by which grain boundary engineering helps to mitigate this problem.
In this study, grain boundary engineering was applied to improve resistance to hydrogen embrittlement in alloy 625 plus, an alloy frequently used in corrosive environments where hydrogen embrittlement is of particular concern. A grain boundary engineered microstructure was successfully produced by applying understanding of the underlying mechanisms of grain boundary engineering. RSL testing demonstrated that grain boundary engineering increased the stress intensity at which failure from hydrogen embrittlement occurred, and caused a shift from intergranular to transgranular crack propagation. These results are discussed in the context of underlying hydrogen embrittlement mechanisms.
Chapter 1: Motivation and Aims

1.1: Motivation

Since its introduction in the 1980s, grain boundary engineering (GBE) has been applied to improve many material properties in polycrystalline materials, including creep resistance, fatigue strength, ductility, and resistance to intergranular corrosion by increasing the presence of low-energy twin boundaries [15]. These methods have been developed empirically by testing a wide range of processing conditions and choosing the best result as the preferred method. These empirical experiments led to two distinct processing routes, known as strain-annealing and strain-recrystallization, with little understanding of the underlying mechanisms.

Recent work has made headway in identifying the underlying processes behind the formation of desirable grain boundary engineered microstructures [14, 19, 20, 21, 22]. It has been found that grain boundary engineering processes are driven by the formation of large, complex, twin related clusters of grains known as twin related domains (TRDs), and that maximizing the size of these TRDs is the most effective way to produce a GBE microstructure. This new approach to GBE has only been applied in a few alloys, and most studies still rely heavily on empirical, guess-and-check methods.

Hydrogen embrittlement is a phenomenon by which the introduction of hydrogen into a metal crystal severely degrades its mechanical properties. It is of particular concern in corrosive environments, such as sour gas wells, where corrosion reactions act as a source of hydrogen. The mechanisms of hydrogen embrittlement are still poorly understood, but one particular mechanism known as intergranular hydrogen
embrittlement can cause a shift from ductile to brittle failure and delayed failure at sustained loads far lower than the yield strength of the material, which can be catastrophic and expensive [31].

Grain boundary engineering has been applied with reported success to limit the effect of intergranular hydrogen embrittlement [26]. However, this is a relatively uncommon application for grain boundary engineering, and the ambiguity behind hydrogen embrittlement mechanisms calls into question the mechanisms by which GBE would be an effective tool for mitigating hydrogen embrittlement.

1.2: Aims

This study aims to apply an understanding of the underlying principle of grain boundary engineering to produce a grain boundary engineered microstructure without the need to test a wide array of processing conditions, and to show that grain boundary engineering can reduce susceptibility to hydrogen embrittlement. Various methods of evaluating grain boundary engineered microstructures will be employed, with emphasis on TRD size as the key metric for ultimate performance. Additionally, analysis of hydrogen embrittled samples will be performed in an attempt to provide insight into the role of grain boundaries in hydrogen embrittlement.
Chapter 2: Background and Literature Review

2.1: Grain Boundaries

2.1.1: Grain Boundary Characteristics

A grain boundary is the interface between two unique crystals, or grains, in a polycrystalline solid. A grain boundary can be fully described with five degrees of freedom, three describing the misorientation angle of the two grains and two describing the plane at which they intersect. The misorientation is often described in terms of a rotation, θ, about a common axis, [uvw]. The boundary plane is often described by the spherical angles θ' and φ'. Two-dimensional analysis typically does not include measurements of the boundary plane, so for the purposes of this study, only the misorientation will be considered [38].

Grain boundaries are generally classified as high-angle or low-angle boundaries, where low-angle grain boundaries (LAGBs) have a misorientation below about 15° and random high-angle grain boundaries (RHAGBs) have a misorientation above 15° [38]. LAGBs are can be described as a discrete array of dislocations, while RHAGBs cannot, due to poor atomic fit between the two lattices. This large misfit between the lattices also results in a much higher boundary energy in RHAGBs than in LAGBs due to a large number of atoms shifted out of their ideal positions, but there are some exceptions to this rule. These exceptions are the result of certain special boundaries that have a high misorientation angle but still have a good atomic fit [3].
2.1.2: The Coincident Site Lattice Model

![Diagram of Σ5 relationship between two simple cubic lattices]

Figure 1: A schematic of a Σ5 relationship between two simple cubic lattices, where the two lattices are superimposed and coincident sites are shown as black dots [1].

These special boundaries are often described using the coincident site lattice (CSL) model. The CSL model uses a parameter Σ to describe the misorientation of a grain boundary. Σ is defined as the inverse of the number of coincident lattice sites if the two crystals were superimposed [39]. For example, a Σ5 means that if the two crystals were superimposed, 1/5 of the lattice sites would overlap. A schematic showing a Σ5 relationship is shown in figure 1. Low Σ grain boundaries typically have much lower boundary energy than RHAGBs, as shown in figure 2 [2].
While the $\Sigma$ parameter does not describe the boundary plane or inclination, it is still useful for understanding the misorientation of two grains and describing special boundaries.

The special boundary with the lowest energy is the $\Sigma 3$ or twin boundary. The twin boundary has mirrored symmetry about a twinning plane. If the boundary plane is parallel to the twinning plane, it is said to be a coherent twin boundary. Coherent twin boundaries have perfect atomic fit at the boundary, and therefore almost zero boundary energy. In FCC materials, coherent $\Sigma 3$ boundaries lie on the close-packed $\{111\}$ planes and take the form of either a $70.53^\circ$ pure tilt along a $<110>$ axis or a $60^\circ$ pure twist along a $<111>$ axis. A schematic of a coherent and an incoherent twin boundary is shown in figure 3.
Deviations from the ideal Σ misorientations can occur as a result of dislocations along the boundary. The maximum allowable deviation for a CSL boundary is known as the Brandon criterion. It is given by the equation

\[ \theta = \theta_0 (\Sigma)^{-\frac{1}{2}} \]

Where \( \theta \) is the Brandon criterion and \( \theta_0 \) is the maximum misorientation of an LAGB (15°) [4]. One consequence of this is that the allowable deviation decreases as the order of the boundary increases.

### 2.2: Recrystallization

When a metal is plastically deformed, strain is added to the material through the formation and movement of dislocations, which increases the energy of the system. This energy can be reduced by two different processes: recovery or recrystallization. Recovery occurs when dislocations of opposite sign come together and annihilate or dislocations of the same sign rearrange into low energy configuration such as sub-grain boundaries. Recrystallization is the formation of a new, undeformed crystal. During recrystallization,
the undeformed grains grow at the expense of the deformed grains around them, driven by the stored energy from plastic strain.

Recrystallization is initiated by one of two distinct mechanisms. Primary recrystallization is a nucleation and growth process in which new orientations nucleate and grow until they impinge on each other. The density of these nuclei depends on the strain and the availability of nucleation sites such as grain boundaries or precipitates, and determines the grain size at the end of the recrystallization process. Several trends in the recrystallization process have been described, and these trends are often referred to as the laws of recrystallization. The following are the laws of recrystallization as described by Burke and Turnbull in 1952 [5]:

1. A minimum deformation is necessary to cause recrystallization.
2. The temperature at which recrystallization occurs decreases as strain increases.
3. The time needed for recrystallization decreases with increasing annealing temperature.
4. The final grain size depends primarily on the degree of deformation, with higher strain resulting in smaller grains.
5. Larger original grain size requires greater strain to give equivalent recrystallization temperature and time.
6. Continued heating after recrystallization is complete causes the grain size to increase.

The kinetics of nucleation and growth are described by the works of Kolmogorov [6], Johnson and Mehl [7], and Avrami [8]. This model, known as the JMAK equation or the
Avrami equation, gives volume fraction recrystallized as a function of time, assuming uniform nucleation, linear growth, and constant temperature, as

$$X_v = 1 - \exp(-Kt^n)$$

where $X_v$ is volume fraction recrystallized, $t$ is time, and $K$ and $n$ are fitted constants.

Strain induced boundary migration (SIBM) occurs when a difference in strain energy across a grain boundary causes the boundary to bulge into the more highly strained grain, leaving an undeformed region in its wake. This undeformed region is still part of the parent grain; however, dislocations are free to migrate into it. A twin boundary can then nucleate behind the migrating RHAGB, resulting in a new unstrained grain. This new grain can then continue to grow in the same fashion as a primary recrystallization nucleus until impingement occurs. The result of this process can be seen in figure 4, a map of kernel average misorientation, which can be considered analogous to plastic strain, in a partially recrystallized sample of alloy 625 plus. The circled region shows where grain boundaries around several strained, twin related grains migrated, leaving an undeformed region in their wake. SIBM typically only happens at a single interface between two grains, however figure 4 shows several adjacent grain boundaries which underwent SIBM at once. This is most likely due to the fact that the grain which were growing are twin related. SIBM typically occurs at lower strains than primary recrystallization, and is differentiated by the existence of a pre-existing parent orientation. This differentiation is subtle and somewhat ambiguous, however, since primary recrystallization nuclei are thought to originate from pre-existing nano-scale volumes [1].
Figure 4: A kernel average misorientation map of a partially recrystallized sample of alloy 625 plus, where recrystallization was initiated by SIBM after a 5% rolling reduction and 2 hour anneal at 925°C. Grain boundaries overlaid with RHAGBs in black, Σ3 in red, Σ9 in green and Σ27 in blue.

2.3: Twin Formation

Annealing twins are very commonly observed in FCC materials, especially materials with low stacking fault energies. Two models exist to describe the formation of annealing twins. In 1969, Gleiter proposed a model for annealing twin formation now known as the growth accident model [9]. This model suggests that twins form when stacking faults occur during the growth of a grain behind a moving grain boundary along a close-packed {111} plane. This process is shown in figure 5, where grain V is growing
at the expense of grain W. Stacking faults occur on parallel \{111\} planes and propagate across the grain, resulting in coherent twins. This model explains the phenomenon that materials with low stacking fault energies more readily form twin boundaries.

**Figure 5:** A schematic showing the formation of annealing twins via the growth-accident model [10].
The other model was proposed by Meyers and Murr in 1978. This model is called the popping out mechanism. In this case, a twin boundary nucleates when an RHAGB dissociates in order to reduce the total boundary energy. This does not require that the RHAGB be moving the way that the growth accident model does [11].

Additionally, the formation of incoherent $\Sigma 3$ and other low $\Sigma$ boundaries must be considered. Other low $\Sigma$ are not annealing twins, but low grain boundaries formed by geometric constraints. When two $\Sigma 3^n$ boundaries meet, the third boundary must also be $\Sigma 3^n$, such that $\Sigma A + \Sigma B = k^2 \Sigma C$, where $k$ is a common factor of $A$ and $B$. This results in combinations such as $\Sigma 3^n + \Sigma 3^{n+1} = \Sigma 3$ or $\Sigma 3^n + \Sigma 3^{n+1} = \Sigma 3^{n+2}$. This is known as the $\Sigma 3$ regeneration mechanism, first described by Randle, et al. [12].

Experimental evidence has supported both of the models described above with some modifications made in order to account for the effect of plastic strain [13]. Field, et al. [45] and Fullman and Fisher [46] have presented evidence in favor of a dissociation method. Jin, et al. performed in situ annealing in nickel and found evidence of growth accident twinning. In 2013, Leff performed EBSD and in situ annealing of copper in TEM and observed both cases of twins forming via the growth accident mechanism and cases of twins forming via the popping out mechanism. This supports the idea that different mechanisms dominate under different conditions. The growth accident mechanism occurs when an RHAGB is migrating during recrystallization or SIBM. However, if an RHAGB becomes immobile and cannot continue migrating, twinning can occur via the popping out mechanism, allowing the more mobile $\Sigma 3$ boundary to migrate and continue the recrystallization process [14].
2.4: Grain Boundary Engineering

Grain boundary engineering (GBE) is the name given to a field which aims to improve the properties of polycrystalline metals by modifying the characteristics of grain boundaries [15]. One way this is done is by promoting grain boundaries with low interfacial energy. The coherent twin boundary, along with other related low-energy CSL boundaries, can be promoted through certain thermomechanical processes (TMP). These processes have been found to produce microstructures with a high density of twin and twin related boundaries, which can improve ductility, segregation resistance, creep resistance, and resistance to intergranular corrosion. These processes have primarily been developed empirically, since the exact mechanisms for twin formation and the formation of grain boundary engineered microstructures are not well understood.

Grain boundary engineering processes that seek to promote the presence of twin boundaries are known as “twin related grain boundary engineering.” Other types of grain boundary engineering seek to improve properties by promoting segregation or precipitation along grain boundaries. This study, however, only focuses on twin related grain boundary engineering, and the terms “grain boundary engineering” and “GBE” will be used herein to refer specifically to twin related grain boundary engineering.

2.4.1: Grain Boundary Engineering Methods

The term “grain boundary engineering” was coined by Watanabe in 1984 [15, 42]. Since then, two distinct methods of TMP have been developed to produce GBE microstructures. These methods are known as strain-anneal and strain-recrystallization [16]. Strain-anneal utilizes low strain (>8%) and annealing at temperatures below the primary recrystallization temperature [17, 18]. Strain-recrystallization utilizes moderate
strain (5-30%) followed by annealing above the primary recrystallization temperature [9]. In 2002, Kumar, et al. determined that sequential TMP is more effective than a single-step processing for producing a GBE microstructure [19]. Subsequently, sequential, or iterative, TMP has been employed in both methods, primarily with the goal of ensuring a uniform GBE microstructure through the full thickness of the sample.

In 2015, Nye performed in situ annealing of copper and observed both primary recrystallization and SIBM at low and high strains. He concluded that low strain conditions and slow recrystallization rates are the best way to promote a GBE microstructure, despite the fact that greater prior strain conditions lead to higher twin density. This suggests that a strain-anneal process driven by SIBM is preferred over a strain-recrystallization process where primary recrystallization dominates [20]. This is also consistent with the findings of Kumar, et al [19].
Figure 6: Summary of processing conditions and resulting CSL length fraction in 317L stainless steel. Samples are labelled as rolling reduction-annealing temp-annealing time [21].

In 2011, Barr tested a wide range of processing conditions in 316L stainless steel, the results of which are summarized above in figure 6, and found that the best way to produce a high fraction of twin boundaries is with a low rolling reduction and a 1 hr anneal at 1000°C (about 70% of the melting temperature) [21].

2.4.2: Evaluating GBE Microstructures

In addition to how grain boundary engineered microstructures form, it is important to consider how we evaluate whether or not a microstructure is grain boundary engineered. The most commonly used metric is the length fraction of CSL boundaries.
Number fraction or density of CSL boundaries is also sometimes considered. However, it has been found that the interconnectivity of CSL boundaries is actually a better predictor of how well a material resists intergranular corrosion, which is often the goal of GBE [41]. This is often quantified by analyzing the triple junctions present in the microstructure. The logic behind this is that a crack propagating along a high-angle grain boundary will be arrested if it comes to a triple junction with two CSL boundaries, but a crack that comes to a triple junction containing less than two CSL boundaries can continue to propagate. Thus, the fraction of triple junctions containing two or three CSL boundaries is a useful metric for describing CSL interconnectivity.

2.4.3: Twin Related Domains

Another way to describe the formation of GBE microstructures is through the growth of large, complex twin related domains (TRDs) [22]. A TRD is a cluster of grains that are all related via twin relationships. A TRD is completely surrounded by RHAGBs and has twin boundaries or other CSL boundaries within it. TRD size, or the ratio of TRD size to grain size, is also a useful metric for evaluating GBE microstructures. CSL boundaries tend to be resistant to intergranular corrosion and fracture, but can still take part in Hall-Petch strengthening. Thus, TRD size can be considered analogous to an effective grain size for corrosion properties, while the traditional twin-limited grain size determines the mechanical properties. TRD size can be challenging to measure, however, since TRDs can be very large and have complex, branched shapes in GBE materials.

TRDs form as a result of multiple twinning events occurring behind a migrating RHAGB. Since there are four \{111\} planes in the FCC structure, a parent orientation can twin to one of four different twin orientations. Each of those can twin back to the original
orientation, or to three other new orientations, leading to the development of a cluster of related orientations. The relationships between these boundaries can be analyzed using a tree notation, developed by Reed, et al. [22] and shown in figure 7. This tree consists of a node for each unique orientation, with lines connecting the nodes representing a $\Sigma 3$ relationship.

![Tree Diagram](image)

Figure 7: A TRD tree diagram adapted from [22].

This notation provides a useful tool for analyzing the complexity of a TRD. Figure 8 shows examples of simple vs. complex TRDs and their subsequent tree diagrams. Since each node in the tree represents a unique orientation, twinning back to the parent orientation does not result in a new node or $\Sigma 3$ relationship. Thus, if twinning only occurs back and forth between two orientations, the tree diagram remains small. However, if the TRD is more complex and contains more orientations, the resulting tree will show the complexity.
During annealing, a primary recrystallization nucleus or an SIBM event will act as the parent orientation, forming growth accident twins as it grows. TRDs will continue to grow until they impinge on each other, and as this growth causes twin boundaries to intersect, higher-order CSL boundaries form as a result of the $\Sigma 3$ regeneration mechanism and further contribute to the complexity of the TRD. A schematic demonstrating this process is shown in figure 9. Thus, a GBE microstructure with the largest TRD size can be produced by processing the material such that the density of recrystallization nuclei is
as low as possible, regardless of whether recrystallization is initiated by SIBM or primary recrystallization. [23]. This is consistent with Nye’s findings that low strains and low recrystallization temperatures produced the best GBE microstructures, since both low strain and low recrystallization temperature will result in a lower density of recrystallization nuclei (or SIBM events).

Figure 9: Schematic showing the formation of a TRD with the twin relationship tree inlaid [23].
In Barr’s 2011 work, he observed that increasing the annealing temperature by just 50°C reduced the final TRD size significantly, as shown in figure 10. This suggests that somewhat small temperature changes can have a noticeable influence on density of recrystallization nuclei and subsequent TRD size.

2.5: Nickel Superalloys

Superalloys are prized for their high strength and corrosion resistance in extreme environments. First developed for use in turbine engines after WWII, their most important properties are long-term strength at high temperatures (above 650°C) and resistance to hot corrosion and erosion. They are usually iron, cobalt, or nickel based and
typically contain significant amounts of chromium to aid with oxidation resistance. They also often contain cobalt, iron, tungsten, molybdenum, and tantalum as major alloying additions and small amounts of carbon [24].

Nickel based alloys utilize solid solution strengthening and precipitate strengthening, with aluminum, titanium, or niobium included to form the strengthening intermetallic phases. Precipitation strengthened alloys usually have the best high temperature performance, with the strengthening phase $\gamma'$, $\text{Ni}_3(\text{Al,Ti})$. These precipitates are highly coherent, having an FCC structure with a lattice constant close to that of the $\gamma$ nickel matrix. The $\gamma''$ phase, $\text{Ni}_3\text{Nb}$, is also an important strengthening phase, as are carbides. $\gamma'$ generally forms cuboidal precipitates in high volume fraction alloys [24]. Some cuboidal $\gamma'$ precipitates are shown below in figure 11.

Figure 11: Cuboidal $\gamma'$ precipitates protruding from a fracture surface.
Nickel Superalloys are attractive candidates for grain boundary engineering, because their low stacking fault energy allows them to twin readily, and they are often used in applications where properties improved by GBE, such as creep or corrosion resistance, are critical. Many GBE studies have been performed on pure nickel and a variety of nickel based alloys and successfully improved the desired properties.

2.6: Hydrogen Embrittlement

The absorption of hydrogen has been found to decrease the ductility and strength of many metals, leading to brittle failures at stresses lower than the expected tensile strength of the material. Almost all metals have some susceptibility to hydrogen embrittlement, but nickel based alloys are particularly susceptible and are frequently used in highly corrosive environments that can provide sources of hydrogen.

Hydrogen can embrittle metals through chemical reactions within the material. The formation of hydrides, in titanium alloys for example, can cause a decrease in ductility through precipitation hardening. Hydrogen can also react with oxygen in some copper alloys to produce water vapor, which fills small voids in the matrix. The pressure build-up can cause brittle failures in this case. Similarly, hydrogen can react with carbon in steel to form methane. However, these chemical reactions are generally not what is being referred to when hydrogen embrittlement is discussed [25].

A number of different mechanisms for how embrittlement occurs have been proposed, but no consensus has been reached. The exact mechanism most likely varies depending on the material and the conditions under which it is being used. The two main
mechanisms studied are decohesion, usually at grain boundaries, and high concentrations of hydrogen causing local plasticity at the crack tip.

2.6.1: Decohesion

Intergranular hydrogen embrittlement is characterized by a transition from ductile to brittle failure accompanied by a loss in strength and toughness. This type of embrittlement is of particular concern because it can cause delayed failure from subcritical cracking at low applied stresses. This can result in unanticipated catastrophic failures and can be difficult to characterize, as failure can take years to occur. Hydrogen ingress is very difficult to prevent due to the high diffusivity of hydrogen, so the best way to prevent this type of failure is to limit the effect it can have on grain boundaries. Hydrogen’s effects on grain boundaries have been studied extensively. Bechtle, *et al.* showed that GBE can reduce susceptibility to intergranular hydrogen embrittlement because CSL boundaries tend to resist segregation and are inherently resistant to brittle fracture [26]. Other studies have also shown that GBE can help prevent intergranular fracture as a result of hydrogen embrittlement [27]. These studies conclude that enhanced hydrogen diffusion at grain boundaries is the primary cause of the intergranular failure and that GBE alleviates this by disrupting the RHAGB network [28, 29, 30]. These intergranular failures are typically attributed to decohesion, as first described by Oriani in 1972 [48], where hydrogen lowers the overall cohesive strength of the crystal. This results in brittle cleavage either transgranularly or intergranularly.

2.6.2: Hydrogen Enhanced Localized Plasticity

In addition to affecting cohesive force, hydrogen can cause localized plasticity near the crack tip and increase dislocation mobility. This effect is highly localized,
occurring within about 1 μm of the fracture surface. The phenomenon, known as hydrogen enhanced localized plasticity (HELP), was first proposed by Beachem in 1972 [31]. Samples that fail intergranularly due to hydrogen embrittlement often have slip traces, dimples, or tears, which are evidence of dislocation interactions near the fracture surface [32, 49, 50]. Examples of these features can be seen in figure 12.

![Figure 12: a) Slip traces and b) dimples on intergranular fracture surfaces, evidence of dislocation interactions at the fracture surface. Adapted from [33] and [34].](image)

The proposed method for hydrogen assisted dislocation mobility is known as the shielding method. In this model, a hydrogen atmosphere forms in the stress field around dislocations and other stress centers. This lowers the interaction energy between dislocations and pinning features, which allows them to move more freely [35]. A plot of the shear stress on one dislocation as a function of distance from another dislocation at
varying levels of hydrogen charging is shown in figure 13 as calculated by Birnbaum and Sofronis [32]. The shear stress decreases with increasing concentrations of hydrogen.

![Figure 13: A plot of shear stress on a dislocation as function of distance from another location at varying levels of hydrogen charging [32].](image)

Robertson observed using in situ TEM deformation that dislocations in titanium were stationary while the stage displacement was held constant. When hydrogen gas was introduced, the dislocations began to move, and new dislocations appeared [34].

HELP is not limited to transgranular fractures and suggests that more may be at play in the case of intergranular hydrogen embrittlement than enhanced hydrogen diffusion and segregation at grain boundaries leading to decohesion. In many cases, a fracture which appears to have propagated intergranularly actually propagated along active slip systems in the vicinity of the grain boundary [49].
Martin, *et al.* observed extensive dislocation cell structures and slip bands on intergranular fracture surfaces in Ni-201 [33]. The dislocation cell structures shown in figure 14 were inconsistent with the relatively low net strain in the samples (about 13%, with a cell size that would be expected for a strain of around 40%). This implies that the interactions between hydrogen, dislocations, and grain boundaries are more complicated than typical grain boundary decohesion. Because of these interactions, the effect of grain boundary engineering on hydrogen embrittlement may also be more complicated than simply disrupting the RHAGB network. One study by Seita, *et al.* showed that twin boundaries in Inconel 725 are resistant to crack propagation from hydrogen embrittlement, but also act as preferred crack nucleation sites. This dual role of twin boundaries is most likely due to interactions between dislocations and coherent twin boundaries, which have a glide plane as the boundary plane. They proposed that crack
nucleation occurs via slip localization at twin boundaries, and then propagates transgranularly via another mechanism [27]. Another study by Koyama, et al. found conflicting results in an austenitic steel. Their results suggested that cracks initiated at triple junctions, and propagated via slip localization along grain boundaries. The slip localization was attributed to precipitates along the grain boundaries [51].

To summarize, GBE has been applied empirically to improve a wide variety of properties, including hydrogen embrittlement. Newer understanding of the underlying processes of GBE, shows that GBE microstructures form via the growth of large complex TRDs. Hydrogen embrittlement is generally attributed to two distinct mechanisms, HELP and decohesion, both of which involve different roles of hydrogen at grain boundaries. Despite efforts to understand GBE and hydrogen embrittlement, many questions still remain to be answered. Gaps in the current understanding of GBE and hydrogen embrittlement include the following:

- New understanding of GBE has not been widely applied to optimize processing parameters.
- Roles of HELP and decohesion in hydrogen embrittlement are not adequately differentiated, especially in the context of grain boundary engineering.
3.1: Alloy Selection

625 plus is an ultra-high strength, highly corrosion-resistant nickel based alloy designed for use in extreme environments, such as sour gas wells. It is an age hardened alloy, with $\gamma'$ as the primary strengthening phase. It is a good candidate for GBE, as it twins readily and is frequently used in environments where corrosion and hydrogen embrittlement are a chief concern for alloy performance. Since nickel has a close packed FCC crystal structure, it is likely to be more resistant to hydrogen diffusion than BCC or martensitic alloys. Since diffusion is enhanced at grain boundaries and other interfaces, it is possible that GBE could help to improve its resistance to hydrogen embrittlement. Its nominal composition is shown in table 1, and a phase diagram and TTT diagram are shown in figures 15 and 16. All material was provided by Carpenter Technologies.

Table 1: Nominal composition of alloy 625 plus [43].

<table>
<thead>
<tr>
<th>Element</th>
<th>Maximum</th>
<th>Element</th>
<th>Maximum</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon (Maximum)</td>
<td>0.03 %</td>
<td>Manganese (Maximum)</td>
<td>0.20 %</td>
</tr>
<tr>
<td>Phosphorus (Maximum)</td>
<td>0.015 %</td>
<td>Sulfur (Maximum)</td>
<td>0.010 %</td>
</tr>
<tr>
<td>Silicon (Maximum)</td>
<td>0.20 %</td>
<td>Chromium</td>
<td>19.00 to 22.00 %</td>
</tr>
<tr>
<td>Nickel</td>
<td>59.00 to 63.00 %</td>
<td>Molybdenum</td>
<td>7.00 to 9.50 %</td>
</tr>
<tr>
<td>Titanium</td>
<td>1.00 to 1.60 %</td>
<td>Columbium/Niobium</td>
<td>2.75 to 4.00 %</td>
</tr>
<tr>
<td>Aluminum (Maximum)</td>
<td>0.35 %</td>
<td>Iron</td>
<td>Balance</td>
</tr>
</tbody>
</table>
Figure 15: A phase diagram, produced in JMatPro with intermetallic phases restricted to $\gamma'$ and $\gamma''$, courtesy of Carpenter Technologies.

Figure 16: TTT diagram for 625 plus produced using JMatPro, courtesy of Carpenter Technologies.
3.2: Surface Study

3.2.1: Sample Conditions

Samples were treated by cold rolling and annealing to the conditions shown in table 2. Samples will be referred to using the naming convention XR_Y, where X is the percent rolling reduction and Y is L, M, or H for low, medium, and high annealing temperature. Annealing temperatures were $0.75T_m$ for medium, $0.75T_m + 25°C$ for high, and $0.75T_m -25°C$ for low. All samples were first solution treated at 1038°C for 2 hours and quenched in water to ensure a uniform starting microstructure.

Table 2: Sample conditions

<table>
<thead>
<tr>
<th>Sample</th>
<th>Rolling Reduction</th>
<th>Annealing Temp (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solution Annealed (SA)</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>5R_L</td>
<td>5%</td>
<td>920</td>
</tr>
<tr>
<td>5R_M</td>
<td>5%</td>
<td>945</td>
</tr>
<tr>
<td>5R_H</td>
<td>5%</td>
<td>970</td>
</tr>
<tr>
<td>10R_M</td>
<td>10%</td>
<td>945</td>
</tr>
<tr>
<td>25R_M</td>
<td>25%</td>
<td>945</td>
</tr>
</tbody>
</table>

The 5R condition was chosen based on the work of Leff, Nye, and Barr [14, 20, 21] to cause recrystallization with a low density of nuclei. The annealing temperature of
0.75\(T_m\) was chosen to produce a favorable recrystallization rate while still maintaining the low density of nuclei, and the variation of 25°C was chosen to find the optimum temperature to produce the lowest density of recrystallization nuclei. The higher strain conditions were chosen in order to highlight the effect of higher densities of recrystallization nuclei on the final microstructure.

3.2.2 EBSD Analysis

Electron backscatter diffraction (EBSD) was performed on the surface of each sample to determine grain size, TRD size, and CSL length fraction. EBSD and all imaging was performed using an FEI XL30 Schottky Field Emission Gun (FEG) Environmental Scanning Electron Microscope (ESEM) with an EDAX/TSL orientation imaging microscopy (OIM) system. Unless otherwise specified, EBSD was collected at a working distance of 15-17 mm, an accelerating voltage of 30kV, a spot size of 5, and a 100 \(\mu\)m aperture, using 4x4 binning and a step size of 1.3 \(\mu\)m. Analysis of EBSD data was performed using the TSL OIM Analysis software package.

Recrystallization was analyzed using kernel average misorientation (KAM). KAM compares the orientation of a point to the orientations of the surrounding points, or kernel, and outputs the average misorientation for each point. KAM can be considered analogous to plastic strain. KAM maps were generated with a scale of 0° to 3° of misorientation. Unstrained, or fully recrystallized samples will have very low KAM, strained samples will have a high KAM, and partially recrystallized samples will have regions of high KAM and regions of low KAM.

Triple Junction analysis was performed using Rohrer Triple Junction Code [40] to evaluate the interconnectivity of CSL boundaries. The analysis classifies each triple
junction according to the type of boundaries it is composed of. A triple junction containing two or three CSL boundaries will be considered resistant to crack propagation, while a triple junction with one or zero CSL boundaries will be considered susceptible. The fraction of triple junctions containing two or three CSL boundaries was reported as the fraction of resistant triple junctions.

3.3: Iterative Processing

Iterative processing was used to observe the formation of a GBE microstructure through the thickness of the material. The 5R_H and 10R_M treatments were repeated three times, with EBSD performed at the surface, the center of the thickness, and in cross section after each iteration in order to observe the propagation of the GBE microstructure through the thickness of the bar. EBSD was also performed on cross sections to ensure that no undesirable anisotropy occurred as a result of the thermomechanical processing. Figure 17 shows how samples were cut from iteratively processed bars.

The samples will be referred to using the naming convention XR_Y_#, where # is the number of iterations. The grain size, TRD size, CSL length fraction, and CSL interconnectivity were collected using the same method described above.
Additionally, one 5R_H_3 sample was double aged at 737°C for 8 hours followed by furnace cool to 721°C for 8 hours. This sample was analyzed with EBSD in order to ensure that an aging treatment would not adversely affect the GBE microstructure by causing excessive grain growth.

3.4: TRD Size Estimation

Quantitative estimates of TRD size in most cases proved difficult to measure, as most conditions had very large TRDs, and a single EBSD scan contained few full TRDs. However, since TRD size is hypothesized to be an important indicator of the successfulness of a GBE treatment, a method of quantifying initial and final TRD size was developed. Arrays of nine overlapping EBSD scans were taken on both the solution annealed sample and the surface of the 5R iteratively processed sample. TRDs were characterized using the TSL software, by ignoring CSL boundaries in the definition of a grain.
For the SA sample, the nine scans were stitched together and the TRD size was measured directly through the OIM Analysis software. For the grain boundary engineered sample, the scans had to be taken at lower magnification in order to include enough TRDs for a statistically meaningful measurement. The lower magnification resulted in some distortion, which made stitching the scans together impossible, and each scan only contained a small number of TRDs, making direct measurement of TRD size from individual scans inaccurate. Instead, the area of each TRD in the array was measured individually. For TRDs fully contained in one scan area, the area was measured directly, using the interactive highlighting tool in the software. For TRDs that spanned more than one scan area, the TRD segments were removed from their respective data sets and stitched together, and then the area of the full TRD was measured. Individual TRDs could be stitched together where full scans couldn’t, because the distortion across one TRD is significantly less than the distortion across a whole scan. These areas were then averaged using Microsoft Office Excel, and an equivalent average TRD diameter was calculated.

3.5: RSL Testing

RSL (Reduced Stepped Loading) testing was used to evaluate the effect of a GBE microstructure on susceptibility to hydrogen embrittlement. Testing was carried out according to ASTM F1624-12 on the 5R_H_3, 10R_M_1, and solution annealed conditions both in air and under hydrogen charging conditions.

RSL testing is a stepped-load four-point bend test on a pre-cracked sample, which produces a threshold stress intensity \( (K_t) \), above which time delayed fracture will occur. Historic methods for testing this threshold were performed using sustained time-to-failure
tests, which could take years to complete. The incremental step loading method used in RSL testing accelerates this method to measure $K_t$ in one week or less [36].

Samples were thermomechanically processed as 1” x 1” x 3” blanks and then machined using electric discharge machining (EDM) to the test specimen dimensions, 0.4” x 0.4” x 2.25”. The samples were notched using EDM at 45° to 0.14” deep and then pre-cracked using a 3-point bending fatigue frame with a stress intensity lower than 35 ksi-in$^{1/2}$ to ensure that no net yielding occurred. Thermomechanical processing was carried out at Drexel University, and all subsequent sample preparation and testing was carried out at Carpenter Technologies.

For each processing condition, two samples were tested in air, and three samples were tested in 3.5% NaCl with a cathodic potential of -1.1 V to induce hydrogen charging. The load was increased by 4 pounds every 3.5 hours, and the load drop was measured at each step. The stress intensity at the final step before the load drop in the hydrogen-charged sample exceeded the load drop in the sample in air was considered to be the threshold stress intensity for delayed failure to occur.

3.6: Post RSL Fractography and Strain Analysis

After failure, the fracture surfaces were examined under SEM, and cross sections were cut from one solution annealed sample and one 5R GBE sample, both in air and in hydrogen charging. SEM imaging was performed on the cross sections just under the fracture surface to examine cracks propagating into the material, and EBSD was performed using 1x1 binning and a step size of 0.9 μm. Nye tensor analysis was performed using the code developed by Leff, et al. in order to evaluate the plastic near
the fracture surface [37]. This method uses the Nye dislocation tensor, \( \alpha_{ij} \), to relate geometrically necessary dislocation (GND) density to the Burgers vector and line direction of the dislocations by the equation

\[
\alpha_{ij} = n b_i r_j
\]

where \( B \) is the Burgers vector, \( r \) is the unit vector, and \( n \) is the number of dislocations intersecting with a unit area normal to \( r \). The Nye tensor is calculated from orientation data using the contortion tensor, \( \kappa \), determined from the least squares fitting of the misorientation of all points within a kernel. GND density is then calculated from the Nye tensor using the following estimation:

\[
\rho \sim \frac{1}{b} \| \alpha \|_1
\]

This is represents the lower bound of the complete dislocation density, as GNDs are only those dislocations that contribute to the curvature of the lattice. Dislocations which do not contribute to the measured curvature of the lattice are known as statistically stored dislocations (SSDs). If two dislocations of opposite sign are within one data collection step, then they will have opposite effects on the curvature of the lattice and the measured misorientation (and thus GND density) will be zero. As the step size approaches the distance between dislocations, the fraction of dislocations which are statistically stored will decrease and the GND density will approach the true dislocation density. The method also assumes that elastic strain has a negligible effect on lattice curvature. The 18 nearest neighbors were used for the Nye tensor calculation, with a 5° misorientation cutoff defined as a grain boundary.
Chapter 4: Results

The results of the initial GBE study are presented to demonstrate that a successful GBE treatment was determined based on KAM, CSL length fraction, CSL interconnectivity, and a qualitative analysis of TRD size. The results of the iterative processing are presented in terms of grain size, CSL length fraction, and CSL interconnectivity through the thickness of the samples. The effects of aging, and a quantitative estimate of TRD size are also presented from this data. The results of RSL testing are presented in terms of threshold stress intensity for hydrogen embrittlement, SEM images of fracture surfaces, and GND density mapping of fracture surface cross sections.

4.1: Surface Study

Table 3: Results of GBE surface study

<table>
<thead>
<tr>
<th>Sample</th>
<th>Recrystallization</th>
<th>Grain Size (μm)</th>
<th>CSL Length Fraction</th>
<th>Resistant Triple Junctions</th>
<th>TRD Size (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SA</td>
<td>n/a</td>
<td>57</td>
<td>64%</td>
<td>38%</td>
<td>-</td>
</tr>
<tr>
<td>5R_L</td>
<td>none</td>
<td>46</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>5R_M</td>
<td>~50%</td>
<td>50</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>
The results of the surface study are summarized in Table 3. The 5R_L and 5R_M conditions resulted in no recrystallization and partial recrystallization, respectively, as shown by the kernel average misorientation maps in Figure 18. Longer annealing times were attempted, and still did not result in further recrystallization. No further characterization was carried out on these conditions, since complete recrystallization is necessary to produce a fully GBE microstructure.

<table>
<thead>
<tr>
<th></th>
<th>Complete</th>
<th>58</th>
<th>84%</th>
<th>58%</th>
<th>-</th>
</tr>
</thead>
<tbody>
<tr>
<td>5R_H</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10R_M</td>
<td>Complete</td>
<td>65</td>
<td>64%</td>
<td>36%</td>
<td>-</td>
</tr>
<tr>
<td>25R_M</td>
<td>Complete</td>
<td>27</td>
<td>50%</td>
<td>23%</td>
<td>47</td>
</tr>
</tbody>
</table>

Figure 18: Kernel average misorientation maps for the 5R_L and 5R_H conditions with grain boundaries overlaid with RHAGBs in black, Σ3 in red, Σ9 in green and Σ27 in blue. A) 5R_L shows no evidence of recrystallization. B) 5R_M shows only partial recrystallization.
The 5R_H condition, however, did result in full recrystallization, and successfully increased the CSL length fraction from 64% to 84% and the fraction of resistant triple junctions from 28% to 58%. TRD size was only reported for the 25R condition, as all of the other scans contained too few full TRDs for an accurate estimate. Nonetheless, the difference in TRD size between the 5R_H condition and the baseline condition is apparent from figure 19, A and B. It is evident that the TRDs in 5R_H are much larger (note the different scale bar in section B) and more complex than the TRDs of the SA condition. The 5R_H process is concluded to be an effective GBE treatment, based on the CSL length fraction, the fraction of resistant triple junctions, shown in figure 18, and a qualitative assessment of TRD size.

The 10R_M condition, shown in part C of figure 19, represents an intermediate between the baseline condition and the 5R_H condition. The higher strain resulted in TRDs that were smaller than those in the 5R_H condition, but modestly larger and more complex than those in the SA condition. The 25R_M treatment caused excessive grain refinement, which resulted in CSL length fraction and interconnectivity less than those of the baseline condition. Figure 20 shows the full triple junction analysis and confirms that the 5R_H process provides the best CSL interconnectivity.
Figure 19: Unique grain color maps ignoring CSL boundaries with RHAGBs overlaid in black, $\Sigma 3$s in red, $\Sigma 9$s in green, and $\Sigma 27$s in blue. This type of map will herein be referred to as a TRD map. A) SA B) 5R_H C) 10R_M D) 25R_M.
4.2: Iterative Study

The 5R_H and 10R_M were chosen for iterative processing to show the propagation of a GBE microstructure through the thickness of a bar. The results are summarized in figures 21 and 22 below.
Figure 21: Graphs showing the evolution of CSL length fraction and interconnectivity with each iteration of processing.
Figure 22: Summary of the grain size measured at the surface center and in cross section for three iterations of the 5R_H and 10R_M processes.

Iterating the 5R_H treatment did successfully increase CSL length fraction and connectivity in the center of the thickness, while still maintaining the same desirable properties at the surface as evident in the top half of figure 21. Iterating the 10R_M process, however, had a less consistent effect, shown in the bottom half of figure 21. CSL length fraction and interconnectivity increased at both the surface and the center on the
first iteration, and then decreased slightly with subsequent iterations. The grain size measurements in figure 22 show that the 5R_H process caused some coarsening of the grain size, but this was deemed small enough to be acceptable, and the 10R_M process increased grain size slightly with one iteration and then decreased back to a similar size to the SA condition. The cross sections showed similar trends to the surface and center, confirming that no unexpected anisotropy was present. Based on these results, the conditions chosen for RSL testing were 5R_H_3 and 10R_M_1.

![TRD map of a 5R_H_3 sample after a double aging treatment](image)

Figure 23: TRD map of a 5R_H_3 sample after a double aging treatment.

After a double aging treatment, the microstructure is relatively unchanged, as shown in the TRD map in figure 23. Some grain growth has occurred, with the average
grain size increased to 91 μm; however, the CSL length fraction is still 80% and the fraction of resistant triple junctions is 46%. Additionally, large, complex TRDs are still present.

4.3: TRD Size Measurement

Figure 24: TRD map of the nine EBSD scans stitched together from the SA sample.
Figure 24 shows a TRD map of the nine EBSD scans from the SA sample. The average TRD diameter is 89.6 μm, the average grain diameter is 40.8 μm, the CSL length fraction is 58.7%, and the fraction of resistant triple junctions is 25.9%.

Figure 25 shows the TRD maps from the nine EBSD scans taken from the GBE sample. Distortion prevented stitching the scans together, so the scans are shown tiled.
together to show where TRDs cross multiple scans. As stated previously, these TRDs were removed from their respective data sets and stitched together separately to manually measure their area. A total of 191 TRDs were analyzed, covering an area of a little more than 6 mm². The area average TRD diameter was 395 μm.

Figure 26: TRD size distributions for the GBE sample by number and area.
The TRD size distribution seen in the top of figure 26 shows a somewhat bimodal trend, with a large number of very small TRDs (<1000 μm²), relatively low numbers of intermediate sized TRDs, and then an increased number of very large TRDs (>100000 μm²). However, when the distribution is normalized by area (shown in the bottom of figure 26), the very small TRDs take up only about 6% of the total area, while the very large TRDs take up over 50% of the area.

4.4: RSL Testing

4.4.1: Threshold Stress Intensity

Table 4: Threshold stress intensity values from RSL testing

<table>
<thead>
<tr>
<th>Sample</th>
<th>Hydrogen charged</th>
<th>Air</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Kt (ksi-in(^{1/2}))</td>
<td>K(_{\text{failure}}) (ksi-in(^{1/2}))</td>
</tr>
<tr>
<td></td>
<td>SA</td>
<td>10R</td>
</tr>
<tr>
<td>1</td>
<td>30.6</td>
<td>32.4</td>
</tr>
<tr>
<td>2</td>
<td>30.5</td>
<td>28.2</td>
</tr>
<tr>
<td>3</td>
<td>25.7</td>
<td>31.0</td>
</tr>
<tr>
<td>Average</td>
<td>28.9</td>
<td>30.5</td>
</tr>
</tbody>
</table>

Table 4 shows the measured values of K\(_t\) from the RSL tests. The 5R GBE condition showed a large increase over the baseline SA condition, while the 10R condition resulted in about the same value as the baseline condition, possibly with a modest increase in K\(_t\).
4.5: Post RSL Fractography and Strain Analysis

4.5.1: Fracture Surfaces

Figure 27: A) An RSL fracture surface tested in air with regions 1, 2, and 3 corresponding to the notch, pre-crack, and ductile failure region with the crack propagation upwards. B) An RSL fracture surface tested in hydrogen charging conditions with regions 1, 2, 3, and 4 corresponding to the notch, pre-crack, subcritical crack growth, and ductile failure region with the crack propagating to the right.

The fracture surfaces each contained several regions. All of them contained a notch, a pre-cracked region, and a region of ductile failure by microvoid coalescence. This region is associated with the final failure, which occurred at the end of the test. An SEM micrograph of a sample tested in air is shown in figure 27 A. One of the ductile regions is shown in figure 29, and one of the pre-cracked regions is shown in figure 28.
The samples tested under hydrogen charging conditions showed a region of subcritical crack growth before the final ductile failure as shown in figure 27 B. This region is characterized by a mixed intergranular/transgranular crack propagation mode.
This region differed between the different processing conditions, with the SA sample (figure 30) showing mostly intergranular fracture. The 5R GBE sample (figure 31), however, showed mostly transgranular fracture, and the 10R sample (figure 32) showed an intermediate mix of both modes.

Figure 30: SEM micrograph of the subcritical crack growth region of the SA sample tested in hydrogen.
Figure 31: SEM micrograph of the subcritical crack growth region of the 5R sample tested in hydrogen.

Figure 32: SEM micrograph of the subcritical crack growth region of the 10R sample tested in hydrogen.
4.5.2: Cross Section Strain Analysis

**Figure 33:** Dislocation density map of the SA air sample cross section with color scale shown in $\log_{10}$ of the dislocation density and x and y axis labels in hundreds of $\mu$m’s. Boundaries overlaid with RHAGBs in black, $\Sigma3$s in red, $\Sigma9$s in green, and $\Sigma27$s in blue.

**Figure 34:** Dislocation density map of the GBE air sample cross section with color scale shown in $\log_{10}$ of the dislocation density and x and y axis labels in hundreds of $\mu$m’s. Boundaries overlaid with RHAGBs in black, $\Sigma3$s in red, $\Sigma9$s in green, and $\Sigma27$s in blue.
Figures 33 and 34 show GND density maps for fracture surface cross sections of both SA and GBE samples tested in air. Extensive plasticity is apparent at the fracture surface, and the strain appears to be more or less uniform.

Figure 35: SEM micrograph of the cross section of the SA hydrogen charged sample where EBSD was performed.
Figure 36: Dislocation density map of the SA hydrogen charged cross section with color scale shown in $\log_{10}$ of the dislocation density and x and y axis labels in hundreds of μm’s. Boundaries overlaid with RHAGBs in black, Σ3s in red, Σ9s in green, and Σ27s in blue. Arrows indicate regions of low plastic strain at the fracture surface.

Figure 37: SEM micrograph of the cross section of the 5R hydrogen charged sample where EBSD was performed.
Figures 35 and 37 show the regions where EBSD was performed on the SA hydrogen charged and GBE hydrogen charged cross sections, respectively, in order to observe the difference in susceptibility to hydrogen embrittlement. Both areas included cracks propagating down away from the fracture surface. The respective GND density maps are shown in figures 36 and 38. Both samples show far less plasticity than the samples tested in air. Some localization of strain at Σ3 boundaries is also visible in the hydrogen embrittled samples. The GBE sample appears to have more continuous plastic strain along the fracture surface, while the SA sample has regions of the fracture surface with much lower dislocation density where brittle fracture likely occurred.
Chapter 5: Discussion

5.1: Surface Study

The initial study provided two important results. The first is that this alloy can be successfully grain boundary engineered, as expected. The second and more significant finding is that a successful GBE processing method was chosen based on the understanding of underlying mechanisms, rather than empirically testing a wide range of conditions and choosing the best. The 5% rolling reduction and subsequent annealing temperatures were specifically chosen to minimize the density of recrystallization nuclei while still resulting in complete recrystallization. Since annealing at 970°C resulted in full recrystallization, and annealing at 945°C did not, even with holds up to 12 hours, we can conclude that 970°C is no more than 20°C above the threshold temperature for recrystallization to occur. This means that 970°C is close to the optimal temperature for minimizing the density of recrystallization nuclei.

5.2: Iterative Study

The iterative processing showed that three iterations of the 5R process were enough to produce a GBE microstructure through the thickness of the bar and that iterating the 10R process did not significantly affect its properties. Cross sections confirmed that the microstructure was isotropic, and an aged sample showed that the aging process did not have a significant adverse effect on the GBE microstructure. It is possible however, that the GBE microstructure could have affected the aging process, by lowering the density of nucleation sites for carbides at RHAGBs, so it should be noted
the double age treatment for a GBE sample likely results in a different distribution of precipitates than the same treatment on a non-GBE sample.

5.3: TRD Size Measurement

Accurate measurements of TRD size proved difficult and time consuming for the GBE condition. The chief problem arises from the extreme size of the TRDs. Even at very low magnification, a single EBSD scan will contain only a handful of full TRDs. The only way to overcome this is to take multiple overlapping scans and then combine them, which is time consuming, and combining datasets can introduce some error as a result of distortion from the lens at such a low magnification. Combining individual TRDs reduces the distortion, but does not eliminate it entirely.

Another problem that arises is inaccurate identification TRDs. The method used only accounts for $\Sigma 3$, $\Sigma 9$, and $\Sigma 27$ boundaries, but higher-order $\Sigma 3^n$ boundaries are present as well. A more complete list of these boundaries and their misorientations is shown in figure 39. These higher-order CSL boundaries almost all have misorientation angles that would be classified as RHAGBs by the TSL software. The effect of this issue can be seen by the high number of very small TRDs identified by the software. Most of these “TRDs” are most likely a part of another TRD, but are separated by a higher-order CSL boundaries at the surface and connected via $\Sigma 3$ relationships beneath the surface, or they are a branch of a larger TRD underneath the surface due to the non-equiaxed morphology of TRDs.

The TRD size reported here represents a lower bound of the true value. A total of 191 TRDs were analyzed in this experiment, 109 of them were less than 1000 $\mu$m$^2$. If
these TRDs were to be ignored, as they are most likely erroneously identified as distinct TRDs, the area average TRD size would increase by about 10 μm in diameter. Only 82 TRDs would remain, which significantly impacts the sample size and distribution.

Figure 39: A list of Σ3 boundaries for $n=1$ to $6$ [44].

5.4: RSL Testing

The results of the RSL test suggest that the GBE microstructure is more resistant to hydrogen embrittlement. The $K_t$ value for the GBE condition is consistently higher than that of the SA condition or the 10R condition. The fracture surfaces confirmed that the 5R condition had the most ductile failure mode, while the SA condition had more brittle failure. A summary of the RSL test results and corresponding microstructures is provided in table 5.
Table 5: Summary of microstructure and RSL test results

<table>
<thead>
<tr>
<th></th>
<th>SA</th>
<th>10R</th>
<th>5R</th>
</tr>
</thead>
<tbody>
<tr>
<td>Grain size (μm)</td>
<td>41</td>
<td>50</td>
<td>81</td>
</tr>
<tr>
<td>TRD size (μm)</td>
<td>90</td>
<td>-</td>
<td>395</td>
</tr>
<tr>
<td>CSL length fraction</td>
<td>64%</td>
<td>74%</td>
<td>79%</td>
</tr>
<tr>
<td>Resistant triple junctions</td>
<td>26%</td>
<td>40%</td>
<td>46%</td>
</tr>
<tr>
<td>$K_t$ (ksi-in$^{1/2}$)</td>
<td>28.9</td>
<td>30.5</td>
<td>42.3</td>
</tr>
<tr>
<td>Fracture type</td>
<td>Brittle</td>
<td>Mixed</td>
<td>Ductile</td>
</tr>
</tbody>
</table>

The dislocation density of the fracture surface cross sections also suggests that the GBE microstructure helped the material to retain its ductility in a hydrogen charging environment.

Several reasons for this result must be considered:

1. Increased ductility overall as a result of grain size effects and the GBE microstructure.
2. The GBE microstructure prevented decohesion at grain boundaries by disrupting the RHAGB network and limiting hydrogen segregation at grain boundaries.
3. The GBE microstructure caused a shift from intergranular to transgranular fracture via HELP by limiting potential intergranular paths for crack propagation.

The increased grain size of the GBE microstructure could potentially impact the results of RSL testing in several ways. The Hall-Petch relationship states that the yield strength of a
material is inversely related to the square root of the grain size. This means that as grain size increases, materials tend to become softer and more ductile. The change in grain size and distribution of RHAGBs also can affect the distribution of precipitates in the sample, resulting in increased ductility by lowering the density of carbides at grain boundaries.

The fact that all three conditions performed the same in air, but differently under hydrogen charging suggests that the results truly reflect an increased resistance to hydrogen embrittlement in the GBE sample, and that simply an increase in overall ductility is not the primary reason for the improved ductility of the GBE microstructure hydrogen charging conditions. However, the stress intensities calculated during RSL testing are not truly reliable after yielding has occurred, since the calculation includes assumptions about crack tip geometry. Hardness testing could be applied to confirm that the mechanical properties of each condition are similar.

Options 2 and 3 are more difficult to evaluate. The difference between them is subtle, and it is possible that both decohesion and HELP are occurring. Previous GBE studies have not mentioned what role HELP may be playing, instead concluding that disrupting the RHAGB network helped to prevent intergranular fracture [26]. The disruption of the RHAGB network almost certainly does reduce hydrogen segregation and diffusion, but the segregation behavior of hydrogen is nearly impossible to observe experimentally, so it is impossible to say definitively what effect the GBE microstructure would have on decohesion at grain boundaries. The results of this study, however, suggest that HELP is playing a role. Some evidence for HELP processes are visible from both the fracture surface images, and the GND density maps.
5.4.1 Fracture surfaces

The intergranular fracture surfaces showed extensive evidence of dislocation interactions, including dimples and slip traces similar to those observed by Martin, *et al.* [33]. These features were found on intergranular fracture surfaces in all three conditions and can be seen in figures 40 and 41. These features suggest that the mode of intergranular fracture is not simply boundary decohesion, but that HELP is occurring.

*Figure 40: Intergranular fracture surface facets from an SA sample with arrows pointing to slip traces.*
5.4.2 GND Density Maps

In the GND density maps shown in figures 33-38 show a large decrease in macroscopic plasticity in the presence of hydrogen. The SA sample shows more embrittlement than the GBE sample, with several facets with very low GND density near the surface. The hydrogen charged samples also show some localization of plasticity, especially at Σ3 boundaries, as shown in figure 42.
Figure 42: Dislocation density map of the 5R hydrogen charged cross section with color scale shown in $\log_{10}$ of the dislocation density and x and y axis labels in hundreds of μm’s. Boundaries overlaid with RHAGBs in black, $\Sigma 3$s in red, $\Sigma 9$s in green, and $\Sigma 27$s in blue. Arrows indicate areas where dislocations are localized around twin boundaries or into subgrain structures.

The fracture in the hydrogen charged SA sample appears to have propagated along RHAGBs while the fracture in the hydrogen charged GBE sample appears to have propagated transgranularly through TRDs. While the crack initiation step cannot be observed in this case due to testing being done on pre-cracked samples, the dislocations interacting with twin boundaries, and the resistance of twin boundaries to crack propagation despite this strain localization are consistent with the conclusions of Seita, et al. [27].

These results cannot confirm whether or not HELP is occurring during intergranular or transgranular crack propagation. HELP is highly localized, and any dislocation structures resulting from HELP would be within about 1 μm of the active slip system, which is too small of an area to resolve using EBSD, meaning that any
dislocations involved in HELP would be statistically stored. The GND density maps can only tell us whether the fracture was ductile or brittle on a macroscopic level and suggest the presence of strain localization, but not confirm the absence of strain localization. However, the fact that \( \Sigma 3 \) boundaries are resistant to crack propagation despite observed strain localization suggests that HELP may not be the only mechanism involved in crack propagation.

Based on these results, it is most likely that a combination of HELP and is occurring at the crack tip regardless of whether the crack propagation is transgranular or intergranular. The GBE microstructure with its large TRD size does not present a path for the crack to propagate intergranularly and that the key mechanism behind the improved performance of the GBE microstructure is the disruption of the RHAGB network, which forces the crack to propagate transgranularly, expending more energy and requiring a higher stress intensity.

**Chapter 6: Conclusions and Future Work**

**6.1 Conclusions**

The key conclusions of this study are as follows:

1. A GBE microstructure can effectively be produced by designing processing parameters based on an understanding of the underlying mechanisms that drive the formation of GBE microstructures, namely the growth of large, complex TRDs.
2. GBE can reduce susceptibility to hydrogen embrittlement by forcing subcritical crack growth to propagate transgranularly.

Additionally, it was confirmed that iterative processing can help a GBE microstructure to propagate through the thickness of a bar, that TRD size can be used as a metric for evaluating GBE microstructures, that an aging treatment does not adversely affect a GBE microstructure, and that significant plasticity is present at a hydrogen embrittled fracture surface, even when the fracture mode is primarily intergranular.

6.2 Future Work

While the GBE processing was a success, additional work needs to be done to refine the methods by which we describe GBE microstructures. The measurement of TRD size needs to be refined in order to better identify TRDs and account for the effect of higher-order $\Sigma 3^n$ boundaries. Obtaining a large enough sample size was a continuous challenge for providing a statistically meaningful estimate of the TRD size. Additionally, due to time constraints, no analysis of the complexity of TRDs was performed beyond CSL triple junction analysis. Generating TRD orientation tree diagrams could help to provide some insight into the complexity of TRDs. An automated method of TRD analysis could help to provide this information, as measuring TRD size individually is time consuming, and manually creating orientation tree diagrams of large TRDs is extremely time consuming.

More work still needs to be done to fully understand the interactions between hydrogen, dislocations, and grain boundaries in order to more effectively combat intergranular hydrogen embrittlement. A holistic study of these interactions is likely
needed, as opposed to studying intergranular hydrogen embrittlement and HELP separately. TEM of fracture surface cross sections from regions of both intergranular and transgranular failure could help to elucidate the role of dislocations in crack propagation. Since hydrogen concentrations are impossible to measure experimentally, modelling of hydrogen segregation behavior at different types of grain boundaries could help to determine if an increased presence of twin boundaries could indeed help to prevent embrittlement apart from simply disrupting the RHAGB network. Analysis of the distribution of precipitates in the GBE microstructure and the effects of this on hydrogen embrittlement should also be performed. Since phase interfaces allow for hydrogen trapping and diffusion, the role of precipitates in hydrogen embrittlement should be studied more thoroughly.

Another area for future work is to apply this processing method to industrial scale processes. 625 plus is generally hot worked, and it remains to be seen if a GBE microstructure can be produced through hot working. This will pose a significant challenge, as current methods of GBE depend on keeping strain and processing temperature low.
References


[36] ASTM F1624-12


