Twin Related Domains in 3D Microstructures of Conventionally Processed and Grain Boundary Engineered Materials

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Abstract

The concept of twin-limited microstructures has been explored in the literature as a crystallographically constrained grain boundary network connected via only coincident site lattice (CSL) boundaries. The advent of orientation imaging has made classification of twin-related domains (TRD) or any other orientation cluster experimentally accessible in 2D using EBSD. With the emergence of 3D orientation mapping, a comparison of TRDs in measured 3D microstructures is performed and compared against their 2D counterparts. The TRD analysis is performed on a conventionally processed (CP) and a grain boundary engineered (EM) high purity copper sample that have been subjected to successive anneal procedures to promote grain growth. The EM sample shows extremely large TRDs which begin to approach that of a twin-limited microstructure, while the TRDs in the CP sample remain relatively small and remote.

Keywords: Grain boundary engineering, 3D characterization, TRD, nf-HEDM

1. Introduction

Microstructural scalar measures have been directly correlated with material performance for a long time. For example, the well-known Hall-Petch scaling relationship [1, 2] quantitatively relates decreasing grain size with increased yield strength. Whereas Hall and Petch did not distinguish between the varieties of grain boundary types, a decrease in grain size necessarily implies more grain boundary area per unit volume. There was also a growing realization that the specific crystallography of individual grain boundaries was of importance for determining materials properties. Grain boundary engineering of face-centered cubic metals and alloys as a concept encompassing an increase in the fraction of boundaries in a microstructure that are special, or associated with a relatively highly ordered crystallographic arrangement [3], was introduced more than 30 years ago [4]. Early research in grain boundary engineering focused on obtaining a similar relationship between the fraction of special boundaries and properties, such as corrosion and arresting of intergranular crack propagation [5].

A scalar measure, the special fraction, has been used as a proxy to differentiate conventionally processed microstructures (CP) from grain boundary engineered microstructures (EM). However, a natural question arises as to what constitutes a special boundary because it is generally understood that the topological configuration of boundaries affects the properties of materials [6]. So, while it is agreed that the topology of the grain boundary network differs substantially between the two types of microstructures, thus giving rise to the improved properties exhibited in grain boundary engineered materials [7], the attempts to quantifiably connect structure with properties are still very much a work in progress.

The experimental observation of crack blunting at $\Sigma 3$ boundaries during intergranular stress corrosion cracking [8, 9] has added yet another layer to understanding the role boundaries play, forcing us to consider the makeup of boundary junctions [7, 10], and how their specific configurations could, for instance, either allow or inhibit crack growth. If we assume all $\Sigma 3$ boundaries will stop crack propagation and all other boundaries will allow it to proceed,
then triple junctions where 2 Σ3s meet will stop the progression of a crack. Knowing the fraction of these special types of triple junctions is more informative than knowing just the fraction of special boundaries. The incorporation of the triple junction distribution (TJD) in the grain boundary network is an initial step toward looking at higher order correlations beyond just grain boundaries, which are representative two point correlations.

Once a triple junction is characterized as impeding crack propagation through the microstructure, then a collection of such objects could form to completely close off any path through the microstructure. The concept of spanning clusters and percolation theory can be invoked to explain transport properties in the microstructure [11, 12, 13]. Below a critical threshold, island clusters form which act as barriers but do not completely rule out a path for the crack to proceed from end to end of the microstructure. A crack or diffusion process is forced to go around these obstacles. However, above a critical threshold, there exists no path around the special clusters that act as barriers. Crack promoting paths form islands within a sea of crack-inhibiting clusters. In 2D, a cluster is said to be percolating if it completely spans the microstructure. If crack promoting boundaries percolate the structure, crack propagation is expected to proceed by way of the shortest path possible. Conversely, if crack inhibiting boundaries like Σ3s percolate the structure, crack propagation can be stunted.

The concept of a twin related domain (TRD) was first introduced by Reed [14] to describe a cluster of grains in which every grain in the cluster is connected to at least one other grain via a Σ3 boundary. The CSL-based group theoretic description implies that every grain in the TRD cluster is related to any other grain in the cluster via a Σ3N relation. The mathematics of rotations resulting from a twin-dominated structure have been studied in a theoretical context [15, 16, 17, 14, 18]. Reed showed a direct relationship between the TRD length scale and material performance [19]. Others who have correlated enhancing of mechanical properties [20, 21], electronic properties [22, 23, 24], and grain growth stagnation [25, 26] with grain boundary engineering processing steps. Given that TRD development is a consequence of grain boundary engineering, these results likely indirectly correlate with TRD development as well. Further attempts to quantify the depth of orientation diversity within a TRD are at the forefront of current TRD characterization [27].

Reed’s matching of TRD length scale to material properties combined information typically derived in 2D from EBSD scans with fracture roughness measurements, a 3D topographic mapping. Since crack propagation proceeds out of plane, the shape of the TRD as an obstacle is of some importance. For grain boundary engineered materials, relatively convex grain shapes in 2D can look drastically different in 3D, taking on non-convex shapes [28]. Stereological assumptions perform poorly in this case. The morphology of TRDs in 3D, whether convex or not, could have implications for percolating paths of cracks, for instance.

To answer some of these outstanding questions, we non-destructively measure the full 3D microstructure of two complementary copper samples, one that has been grain boundary engineered and the other conventionally processed. Since microstructures are never static the two samples were subjected to the same annealing treatment and re-measured to study the evolution of the TRD populations. These observations are interpreted in the context of common microstructure metrics and also in the context of standard 2D measurements. The implications of these results are then considered in the context of experimental resolution limitations, operational definition of the clusters, possibility of TRD fragmentation, measured special fractions, and expected critical thresholds.

2. Methods

2.1. Experimental Measurement

In this study, two physical samples of pure copper were studied through several stages of annealing. Initially 1.1 mm diameter cylindrical samples of conventionally processed (CP) and grain boundary engineered (EM) copper were produced with similar grain sizes. The CP sample had an average sphere-equivalent diameter grain size of \(<d> = 18.2 \mu m\), and the EM sample had \(<d> = 24.4 \mu m\), initially. These samples were then experimentally mapped using the near-field high-energy diffraction microscopy (nf-HEDM) [29, 30, 31] technique at Sector 1 of the Advanced Photon Source at Argonne National Laboratory allowing for interrogation of 0.4 mm³ volume. The measurement volume is limited by the allotted beam time at the facility. The crystallographic orientation data was then reconstructed from the X-ray scattering data using the IceNine forward modeling package [32] resulting in 0.4 mm³ total volume at a resolution of 2 μm × 2 μm × 4 μm. Each volume represents ~10⁷ individual data voxels with unique crystallographic orientation. Taking advantage of the fact that nf-HEDM is a non-destructive technique, we were able to repeatedly map
the same physical volume multiple times. We were able to map both samples before and after annealing (at identical conditions for 2 hrs at 500 °C with flowing inert gas). Due to the limited beam time allotment at the experimental facility, only the EM sample was mapped for a second, additional anneal step under identical conditions. Figure 1 represents a 3D rendering of the two measured microstructures in the initial state.

2.2. Data Analysis

For each of the 5 measured and reconstructed volumes, referred to as CP Anneal 0, CP Anneal 1, EM Anneal 0, EM Anneal 1, and EM Anneal 2, a 3D grain map was defined such that each voxel is assigned a grain ID which signifies spatially connected voxels misoriented from each other below some threshold value, in this case \( \leq 2.5^\circ \).

All grains with a diameter less than 5 \( \mu m \) were excluded. This minimum volume cutoff criterion is commensurate with the measurement resolution. For simplicity, the specific grain morphology was ignored and only the grain topology was considered. For ease of analysis, we abstractly represent the microstructure data by a grain graph, which is constructed by designating grains as vertices and grain boundaries as edges. The graph includes information such as grain ID, average orientation, and volume associated with the grains, and pairs of grain IDs associated with grain boundaries. Finally, grain boundaries were identified and labeled as a \( \Sigma 3 \), a \( \Sigma 9 \), or \( \Sigma 27 \) based on their corresponding disorientation, \( \Delta g = g_A^{-1}g_B \), where \( g_A \) and \( g_B \) are the orientations of the grains on the two sides of the boundary.

A boundary is classified as the \( \Sigma 3 \), \( \Sigma 9 \), or \( \Sigma 27 \) if they are within \( \leq 0.5^\circ \) misorientation from their corresponding disorientation operator. Note that only boundaries that could be classified as either \( \Sigma 3 \), \( \Sigma 9 \), and \( \Sigma 27 \) were included in this study, the \( \Sigma 3^N \) types. The use of boundary classification criteria more conservative than the Brandon criteria was justified here to include only those boundaries which most likely exhibit “special” properties [33]. Incorporation of boundaries not close to the \( \Sigma 3^N \) descriptor could have the small and unlikely chance to drastically skew the sizes of TRDs since TRDs represent connected components. Recall TRDs are simply clusters in the grain graph where \( \Sigma 3 \) boundaries are connecting edges. Our objective was to minimize the number of false positive identifications of boundaries as connecting edges for cluster analysis.

To define twin-related domains, a search was conducted on the grain graphs starting at a randomly seeded grain and marching out along labeled \( \Sigma 3 \) edges until no more grains are added to the defined TRD. Those grains were associated with a single TRD and removed from the pool of available grains to be associated with TRDs. The process was continued until all grains were associated with an individual TRD. In some cases a TRD would contain only a single isolated grain. Even for the largest grain map (~50k grains), the process of labeling TRDs took less than 1 minute using MATLAB\textsuperscript{TM}. This processing step scales primarily with the number of grains. Further, the 3D structure was separated into 2D sections and the same TRD identification conducted on those sections individually.

Note that TRDs defined here is commonly referred to as connected-components, and the algorithm described above is commonly referred to as “breadth-first search” [34]. Connected-components may be considered as a special case of cluster analysis with binary equivalence, or cluster relationship (two grains belong to the same TRD if they are connected by a \( \Sigma 3 \) boundary). Alternatively, we may define the equivalence relationship to include \( \Sigma 3 \) and \( \Sigma 9 \), which will denote as \( \Sigma 3^2RD \) clusters. Finally, a similar cluster analysis was performed allowing for all \( \Sigma 3s \), \( \Sigma 9s \), and \( \Sigma 27s \) to define clusters, called a \( \Sigma 3^3RD \) here. In this naming convention, a TRD is exactly a \( \Sigma 3^3RD \).

To investigate the connection between special boundary fraction, \( f_\Sigma \), and the cluster size, we numerically estimated the TRD size as a function of \( f_\Sigma \) by randomly sampling all possible boundary configuration for the measured grain boundary network. This is analogous to the computational methods used in percolation theory [35]. As a concrete example, given the measured boundary network extracted from the measured microstructure, each boundary is re-assigned as “special” with some probability \( p \) determined by \( f_\Sigma \). Clusters are then identified, and their sizes tabulated. By randomly sampling sufficient number of configurations, i.e., running enough independent simulations, we would arrive at an ensemble averaged cluster size for each value of \( f_\Sigma \). This method is generalized to all \( \Sigma 3^NRD \) with the corresponding \( f_{\Sigma^n} \), \( \Sigma 3^N \) boundary fraction.

3. Results & Discussion

3.1. 3D Results

The boundary number and triple junction number fraction, \( f_\Sigma \) and \( J_N \) respectively, for the measured microstructures are presented in Table 1. Again, only \( \Sigma 3 \), \( \Sigma 9 \), and \( \Sigma 27 \) are considered for both the \( f_\Sigma \) and \( J_N \) calculations in this
manuscript. The particular distribution observed in the boundary and triple junction of the EM sample suggests that
special boundaries and junctions ($J_1$) are not distributed isotropically across the sample. Specifically, $J_1$ population is
expected to be greater than $\frac{1}{3}$ of $J_1$ if special boundaries are clustered together [12]. In fact, this is consistent with the
analysis of the same data set presented by Li et. al. [28], which shows a considerable fraction of the quadrupole nodes
are coordinated by more than five special boundaries, implying special boundaries are likely connected to each other.
Note, however, that the same cannot be inferred from the CP sample.

Table 2 summarizes the statistics of TRDs extracted from the experimentally measured 3D microstructures. TRD
identification uses only $\Sigma 3$s to define connectivity within a TRD, as is consistent with the definition of a TRD. Focus
is particularly paid on the largest TRDs as defined by the number of grains in a given collection. The size of the
TRDs seen in the EM sample is remarkably large. Within the same volume of measurement, a TRD in the EM sample
contains nearly 10 times as many grains as the largest in the CP sample, despite the significantly larger number of
gains in the CP sample (factors of $2^{\sim}5$). For example, the largest TRD in the EM sample contains 1395 grains
(Table 2), or more than 10% of the entire measurement volume and a sphere-equivalent diameter of 460$\mu$m.

In some cases, the TRDs extend to the edge of the limited height of the measurement volume. For example, Figure
2 shows the extent of the five largest TRDs within their measurement window (outlined in grey) and capped above
and below. Each TRD is falsely colored by a TRD ID. For the EM material, the sheer size of the largest TRDs makes
it likely (and is indeed the case) that they are not fully measured in the $\sim400\mu$m tall measurement window. In an
attempt to capture the full TRDs, we have extended the height of our measurements volume in the later anneal states.
However, this leads to the seeming increase in size of the largest TRD in both the CP and EM samples between initial
measurement (Anneal 0) and later measurement (Anneal 1).

Given the large TRD size observed in the EM sample, it would be interesting to investigate the orientation diversity
within the TRDs. This could be studied by examining the twin ordering. In particular, Reed [17, 14] and Cayron
[18, 36, 27] have accomplished this by reconstructing the TRD twinning tree. Note that, as described in the literature,
twinning tree construction is inherently ambiguous, as the designation of the central grain, or the root of the twinning
tree is not unique. One convention is to designate the orientation at the center of mass position of the TRD as the
twining base [27].

If the tree is symmetric about this orientation, one can safely say that the selected central grain is most likely the
nucleus from which the TRD formed through isotropic twinning. We have chosen instead to calculate the betweenness
centrality [37] for each node in a given TRD, as it is unbiased to grain size or TRD shape. Betweenness centrality
counts the number of times a given node is included in a shortest path between pairs of nodes. The grain with
the highest betweenness centrality then represents the grain which the most pairs of grains in the TRD must traverse
when stepping through the TRD along $\Sigma 3$s. Figure 3 shows the reconstructed twinning tree for the largest TRD
in the EM sample across annealing treatments. Note the using the grain associated with the maximum betweenness
centrality finds the same central orientation, as the trees are very similar.

With the twinning trees fully constructed, we compute the more advanced metrics of TRDs as proposed by Cayron
[27], such as the length of the longest chain ($LLC$) and polysynthetism ($p$). $LLC$ quantifies the largest twinning order
present within a TRD, while polysynthetism quantifies the average degeneracy of unique orientations found in a TRD.
The extent of the twinning order is visually apparent, and it is larger than any reported to this point. Table 4 represents
the calculated values for $LLC$ and $p$ in the two samples. It is particularly noteworthy that a $LLC_{\text{max}}$ of 23 is measured
in the EM sample. There exists a pair of grains in the TRD with a $\Sigma 23$ misorientation, an impressively long twin-
chain. Interestingly, the polysynthetism differs depending on the processing method (grain boundary engineering vs
conventional processing) of the same type of material. This implies that reverse twinning is slightly more preferred in
the EM sample.

Figure 4 presents the same nominal 2D slice of the measured EM volume at successive anneal states. Here, we
have visualized the same slice as a grain map (Figure 4(a), (d), (g)), a TRD map (Figure 4(b), (e), (h)), and a non-
$\Sigma 3^N$ boundary network map (Figure 4(c), (f), (i)). Since grain orientation changed minimally between anneal states,
correspondence between colors in the grain map is expected, as the colors map directly to crystallographic orientation.
The similarity of TRD colors amongst the three anneal states is merely coincidental to the color selection scheme of
the TRDs, as the color of the TRD is chosen to be the color associated with the orientation of the largest grain in the
TRD.

Upon close visual inspection of Figure 4, one finds that the removal of just one carefully chosen $\Sigma 3$ boundary
can partition a single TRD into smaller TRD fragments. We will refer to the process of counting a single TRD as
multiple TRDs as fragmentation. It is possible for fragmentation to occur as part of measurement artifact or physical processes. In the case of measurement artifact, spatial resolution limits of microscope could lead to misidentification of grains. The lack of access to 3D data would result in incomplete connectivity information unrecoverable from most statistical means [38]. On the other hand, grain coarsening could lead to erosion of TRDs, which could also lead to fragmentation. TRDs found in an annealed sample could very well belong to the same parent TRD in the sample prior to thermal treatment. Note that the nature of fragmentation in 2D is different than that in 3D; it is much easier to disconnect a TRD in 1D compared to 2D, and similarly in 2D compared to 3D. Visually the number of multiple TRDs as fragmentation is quite clear, corroborating the earlier assessment about $J_3$ populations in the EM.

### 3.2. Relation to 2D results

Given that the 3D data produced with nf-HEDM originates from a collection of consecutive 2D slices, each comprised of a physically measured orientation map from nf-HEDM, it is possible for us to directly analyze the original 2D data. We have applied the TRD identification procedure described above to the 2D orientation maps. Characterization similar to that of Table 2 for the 2D data is presented in Table 3. Since independent analysis is performed on each 2D section, inter-layer averaged values are presented in Table 3. Variations across layers are represented by the standard deviation of the quantity across the many layers.

As with the analysis in 3D, particular attention is paid to the aggregate statistics of the largest five TRDs, which accounts for a significant fraction of the measurement volume. In terms of both number fraction, the aggregates measured in the 2D analysis are congruent with the 3D analysis to within the analysis variation. The same can be said between the correspondence of area and volume fraction. This is particularly encouraging, as access to 2D measurements are often abundantly available. We should note that tracking only the largest TRD in 2D does not provide the same level of robust estimate of their 3D counterparts. This is not surprising, as the shapes of TRDs are far from uniform. Individual cross section easily misidentifies the largest TRD of the measurement volume. The slight but systematic suppression of the 2D number fraction may be attributed to fragmentation of TRDs during the analysis process, which may be addressed in a procedure described in the next section.

In general, bias observed in estimates from 2D data should not be surprising, as TRDs generally violates the assumption of rotational symmetry in stereological estimates [39]. This can be seen directly in Figure 2 from the 3D morphologies. Figure 5 presents an example of two slices of the EM material at vertical positions offset by 40 $\mu$m. While the four TRDs, indicated by white ‘x’s, produced by the 2D analysis are in fact part of the same TRD connected in 3D, they have been identified as distinct TRDs. They are, however, clearly still crystallographically related. More specifically, the misorientations between pairs of grains within a TRD belong to a group whose generator is the $\Sigma^N$ relationship. We will define grains satisfying this criteria to be crystallographically consistent. If two grains from two spatially separated TRDs are crystallographically consistent, then their encompassing TRDs are likely to belong to the same parent TRD. One could take advantage of this fact and check for crystallographic consistency between pairs of grains within spatially separated TRDs. Under a restricted set of assumptions, two spatially separated TRDs with grains related by a $\Sigma^N$ relationship must belong to the same parent TRD. Following this line of thought, we will define a statistical model for deciding whether two TRDs are crystallographically distinct in the next subsection.

### 3.3. Crystallographically distinct TRDs

Since we are looking at the thermal evolution of our measured 3D microstructures, we are inspired by Figure 5 to ask the following: can we determine if two separately identified TRD clusters are likely to be part of the same TRD in an earlier anneal state? While none of the distinctly labeled TRDs in the EM sample are physically connected through a $\Sigma$ boundary, it is conceivable that they were part of a larger TRD which has undergone erosion during the mechanical processing. For example, surrounding grains could erode into the TRD as they coarsen during thermal annealing. In this case, the parent TRD at an earlier point of the processing history would be even larger than what is currently reported here. An example of this can be found in our measurement. One could imagine the large TRDs shown in Figure 2 being derived from a single TRD at an earlier processing step, and erosion of the TRD causing it to fragment into several smaller TRDs.

A similar analysis taking advantage of crystallographic consistency between grains amongst TRD was already presented in a previous section. Spatially separated TRDs in a 2D cross section were identified and associated to belong to the same TRD in 3D. In this section, pairs of TRDs that are likely to be part of a single TRD will be
called “crystallographically indistinct”, while those likely formed independently will be called “crystallographically distinct”.  

In order to construct a statistical model, we must additionally quantify the likelihood for two randomly selected grains to satisfy our crystallographic consistency requirement. In other words, we would like to define a statistical model based on the collection of individual likelihoods of grain pairs being related through a $\Sigma^3N$ on chance alone. This is to capture the fact that probability for grains that belong to the same TRD to be related is much higher than expected randomly.  

We start out with the assumption that two pairs of grains (grain i and grain j) are completely uncorrelated and define a probability that they are uncorrelated/randomly associated.

$$\delta q_{ij} = \Delta g(q_i, q_j)$$  

$$p_{Random,ij} = \frac{[\Delta g(\delta q_{ij}, \delta q_{\Sigma^3N})]}{15\sqrt{3}N}$$  

$$p_{Random,ij} = \min(p_{Random})$$  

$$p_{\Sigma,ij} = 1 - p_{Random}$$  

First, the disorientation between those two grains, $\delta q_{ij}$, is computed. Next, a list of the angular distances, $p_{Random}$, between that disorientation and all of the $\Sigma^3N$ variants scaled by the appropriate Brandon criteria, $15\sqrt{3}N$, is computed. The minimum distance is then associated with the probability that the two grains are unrelated, called $p_{Random,ij}$. If this number is greater than 1, it is set to 1. Conversely, the probability that the boundary is a just the complement of it being random $\left( 1 - p_{Random,ij} \right)$.  

This probability is then computed individually between each of the $N_1$ grains in TRD$_1$ with each of the $N_2$ grains in TRD$_2$. If we again start at the assumption that the grain pairs in different TRDs are completely random, then we expect the collective product of those random events to also be random. The following equation,

$$p_{random} = (\prod_{i=1}^{N_1} \prod_{j=1}^{N_2} p_{Random,ij})^{\frac{1}{N_{TRD}}}$$  

defines a collective measure that the original assumption of crystallographically distinct TRDs is true. It is simply the geometric mean of all of the individual grain pair comparison terms $(p_{Random,ij})$.  

Next, a threshold, $p_{thr}$, is set. For the case where $p_{Random} \geq p_{thr}$, the original assumption that the chosen pair of TRDs are crystallographically distinct is accepted. When $p_{Random} < p_{thr}$, the TRDs are deemed crystallographically indistinct, and may likely have been part of a single TRD at some point.  

Practically performing this procedure has some computational costs that need to be considered. For a single pair of TRDs chosen, this process scales as the product of the number of grains chosen from each TRD and the number of variants $\Sigma^3N$ variants used. As N is increased, the number of variants rapidly rises, $\ N_{variants} \propto 4 \times \sum_{i=2}^{N} 3^{i-1}$. For $N = 10$, this will amount to over $100k$ entries in $p_{Random,ij}$. In most cases when comparing large TRDs with large TRDs, for all intents and purposes it is possible to sample several grains from each to decide if they are crystallographically distinct using the full list of grains for both as the value of $p_{random}$ tends to converge. Since this could be performed for every possible TRD pair, the number of evaluations will then scale proportionally to the square of the number of TRDs in the volume ($\propto N_{TRD}^2$).  

To determine whether the proposed metric is a good statistical discriminator for crystallographic distinct-ness, a test was performed on the TRDs extracted from the experimental EM sample. Using TRDs which consist of more than 10 grains, $p_{random}$ was calculated for all possible pairs of TRDs and as a function of $N$ in $\Sigma^3N$ from 5 up to 10. Next, TRDs were split into two TRDs and $p_{random}$ was calculated for multiple different cuts for all of the TRDs as a function of $N$ from 5 up to 10. This population defines what $p_{random}$ would be for pairs of crystallographically indistinct TRDs. Figure 6 presents the results of each study in shades of blue and shades of gray, respectively. The dashed red line indicates a value of $p_{thr} = 0.8$ where almost all (99.7%) of split TRDs fall below this value and 99.95% of all
randomly compared TRDs fall above this value. Since we know the split TRDs are crystallographically indistinct, the gray curves represent how the collective measure might vary when comparing TRDs that might be considered as a single TRD. The various shades of each color spectrum indicates that there are diminishing returns for allowing cutoffs above \( N = 5 \). This intuitively makes sense as the Brandon criteria is used as a normalizing distance metric. However, as \( N \) goes up, this criteria starts to approach the measurement resolution. If one is really interested in the length scale of the TRDs, this method would ensure that the topological connection between collections of grains could be repaired from noisy or incompletely geometry using the structure of the \( \Sigma 3^W \) group. The statistical comparison of TRDs in the EM sample did not indicate that the observed large TRDs should be merged. This indicates that they likely formed independently. This method does, however, still aid in grouping TRDs from 2D data or in successive 3D measurement if the large TRDs begin to erode and fragment.

3.4. Cluster Size Dependency on \( f_s \)

In this section, we will focus on the differences between the two measured samples. We would like to know if the network topology of the EM sample is drastically different from the CP sample. The percolative model provides a simple one-parameter measure of topology [35]. We will accomplish this by defining the critical special boundary fraction, \( f_s^* \), the special fraction in which large clusters begin to develop in the measured microstructure’s network. This will be performed independently of the observed crystallography of the boundaries.

Since the EM sample has large percolating TRDs, we will try to systematically remove special boundaries from the observed population to see how far above the critical threshold the sample is. If the microstructure is just barely above this critical point, removal of only a few special boundaries will have the effect of breaking up the large TRDs. We will use the observed special boundaries referring to \( \Sigma 3s, \Sigma 9s, \) and \( \Sigma 27s \). We will reduce the observed special boundary population until the EM sample has near or lower special fraction than the CP sample, allowing comparison of cluster sizes of the same microstructures with now effectively the same special fraction.

3.4.1. Prediction of cluster size given known \( f_s \)

Given the disparate differences in observed TRD sizes between the EM and CP sample, are these TRD size differences predictable from the measured special fraction of \( \Sigma 3s \)? We know from Table 1 that these two samples have slightly different \( f_s^* \) values. Therefore, one could ask what cluster sizes might be in the two samples if boundaries were labeled randomly as connecting. One could then map any special fraction to a predicted cluster size. Would these results be in good agreement with observation? If the cluster sizes predicted at the measured \( f_s^* \) for the two samples agree with the observed TRD sizes, one can likely assume that random arrangement of \( \Sigma 3s \) tells the whole story, and \( f_s^* \) is a good predictor of the TRD sizes.

We use the concept of a percolation threshold, a single value, as a proxy for topology because lattices with different topologies exhibit different critical thresholds. In percolation theory, the critical fraction of boundaries labeled as connecting is highly dependent on the topology of the microstructure network. As a reference microstructure, an equivalently sized (in volume and number of grains) synthetic Voronoi microstructure is generated. We then perform a systematic study to look at the size of the largest cluster as a function of varying \( f_s \) in the EM, CP, and Voronoi microstructures. The largest cluster size is tabulated for \( 1k \) test configurations by randomly selecting boundaries and labeling them as connecting or not with probability, \( p = f_s \). \( f_s \) is varied from 0% to 100% in increments of 0.25%. This represents \( (6 \text{ microstructures}) \times (400 f_s^2) \times (1000 \text{ permutations}) = 2.4M \) total random configurations tried. Figure 7 shows the results up to values of \( f_s \) before clusters begin to fully connect, defined here as clusters approaching a size of \( 1k \) grains. We see that the size of the largest cluster rapidly rises around different values of \( f_s \) in each of the three different microstructures (two experimental and one synthetic). Clusters will include over \( 1k \) grains at as low as \( f_s = 6\% \) for the EM sample, whereas it is closer to 8% for the CP sample and even higher at 11% for the Voronoi microstructure. Quoting a critical threshold allows us to compare when one would expect a microstructure to percolate from a random construction of \textquoteleft\textquoteleft special\textquoteright\textquoteright connecting boundaries to that which is actually observed. Interestingly both samples are above a critical threshold if special boundaries were in fact randomly assigned, yet the CP sample does not develop large TRDs typically expected of it with just random assignment of special boundaries.

We have seen that the observed TRD sizes in the CP sample is surprisingly lower than would have been predicted from random assignment of the \( \Sigma 3s \) present, whereas the large TRDs sizes in the EM sample do not necessarily rule out random assignment to fully explain the observation. Random assignment of the \( \Sigma 3 \) boundaries in the CP sample
would have predicted much larger TRDs than is actually observed; the observed TRD sizes is more consistent with a significantly lower special fraction. This suggests that the Σ3s are more evenly distributed throughout the microstructure. It is not consistent with their arrangement being clustered together. However, we cannot conclude anything about the arrangement of special boundaries in the EM sample.

3.4.2. Cluster sizes after removing boundaries

Both the fraction and arrangement of special boundaries play a role in the length scale of the observed TRDs. The question still remains as to whether the special fraction can explain the differences in TRD sizes observed. The fraction of special boundaries in the EM sample could be so high that the spatial arrangement barely matters, and the emergence of large TRDs is expected without knowing anything about their arrangement. Another approach to understanding how the observed boundaries within the network are clustered would be to employ those measured over a random construction, as was done in the previous section. Borrowing from percolation theory, perhaps the EM sample has a special fraction large enough that large TRDs are expected. On the other hand, if the EM sample somehow had the same special fraction as the CP sample, but the EM sample still exhibited large TRDs and the CP sample did not, this would imply that their special boundary arrangements were significantly different. For a fixed $f_{\Sigma3}$ in the case of large TRDs, we would infer spatial clustering of Σ3s; in the case of small TRDs, we would infer the converse – significantly less clustering.

Next we want to answer if the EM sample had the same $f_\Sigma$ of observed boundaries as that of the CP sample: would their $\Sigma^3$RD clusters (TRDs, $\Sigma^3$RDS, $\Sigma^3$RDs, etc) be much smaller? It is possible that the removal of only a few boundaries could significantly impact the observed cluster sizes. So we systematically down-sample the measured special boundaries ($\Sigma^3$s, $\Sigma^9$, and $\Sigma^{27}$s) from the EM sample to match or be below the $f_\Sigma$ found in the CP sample. This is an attempt to retain boundaries known to be special, which is slightly different than the earlier exercise of random assignment. Figure 8 represents the largest $\Sigma^3$RD cluster size in the EM sample as special boundaries in the sample are down-selected such that the special fraction falls in the range, $0 \leq f_\Sigma \leq 0.25$. One simply cycles through all special boundaries and keeps a boundary labeled as special if a randomly chosen number between 0 and 1 from a uniform distribution is less than $\frac{f_{\Sigma,Target}}{f_{\Sigma,CP}}$. The case where $(f_{\Sigma,Target} = f_{\Sigma,CP} = 20 - 24\%)$ is an attempt to control for $f_\Sigma$ even if the topologies of the two experimentally measured samples are different. We find the largest $\Sigma^3$RD cluster is still large even when the reduced special fraction of observed boundaries in the EM sample is closer to that of the CP sample ($f_\Sigma = 23\%$). The largest $\Sigma^3$RD size is $1054 \pm 22$ grains in this particular case. This is particularly interesting when we recall that the total number of grains in the EM sample is smaller than that of the CP sample. From this result, it is clear that $f_\Sigma$ alone cannot be used as a reasonable predictor of $\Sigma^3$RD cluster sizes.

Considering we found that the $\Sigma^3$RD cluster size is not affected by randomly removing close to half of the special boundaries for the EM sample, one could ask if the large clusters would be more prone to being split up if the existing special boundaries were removed in a more systematic way. We also explored the size of $\Sigma^3$RD as $N$ is varied. Table 5 indicates that the largest $\Sigma^3$RD does not change much in size with inclusion of boundaries other than $\Sigma3$ as special in $\Sigma^3N$. This is in good agreement with a TRD being purely defined by $\Sigma3$s, and the other $\Sigma^3N$s with $N \geq 2$ in the TRDs being a direct crystallographic consequence of closure and $\Sigma^3N$ forming a group.

Here we have shown that when reducing the special fraction of boundaries, defined as $\Sigma3$s, $\Sigma9$s, and $\Sigma^{27}$s, from the EM sample by removing only observed special boundaries, the $\Sigma^3$RD remains large even after reducing the fraction to that or below the observed value of the EM sample. This strongly implies that when putting EM and CP samples on similar special fractions, their arrangement of special boundaries favors clustering and uniform arrangements, respectively.

4. Conclusion

The three-dimensional polycrystal crystallography, geometry, and topology of two copper samples has been measured at successive annealing stages using the nf-HEDM technique, resulting in large volumes of size 0.4mm$^3$ at close to $\mu$m resolution. The topology and crystallography information is used to define more highly coordinated grain structures like the twin-related domain (TRD). We have explored the largest TRD sizes in the two samples as a function of annealing and special fraction.
The main findings presented here include the observation of extremely large TRDs in the EM microstructure in 3D which include more than 1k grains and over 10% of the measurement volume. These large TRDs were relatively resistant to being fragmented during coarsening. We concluded that the large TRDs probably formed independently since they are deemed crystallographically distinct. Differences in observed TRD sizes across samples are most likely due to way $\Sigma 3$s intersect in the EM sample and not in the CP sample. Vast differences of TRD sizes could not be explained purely on the basis of either the number of grains in the system, observed special fraction, or critical threshold. TRD statistics from 2D agree reasonably well with those from 3D, and a model was presented to infer connectivity of TRDs when incomplete information of the grain boundary network exists. Statistical descriptions such as TJD, and likely QND, are found to be better indicators of the emergence of connected structures while special fraction is not.

The development of TRDs in grain boundary engineered microstructures demonstrate how $\Sigma 3$ boundaries alone cohesively connect the network evidenced by the large fraction of $J_3$-types. Conversely, $\Sigma 3$ boundaries remain mostly insular in conventionally processed microstructures seen through a large fraction of $J_1$-types. It is the large intersection of $\Sigma 3$s inherent in the EM, but missing in the CP microstructure, that gives rise to the differences in observed TRD sizes. The $\Sigma 3$ boundaries in the EM microstructure connect with each other and the rest of the microstructure fundamentally in a different way than those $\Sigma 3$ boundaries do in the CP microstructure.

Acknowledgements

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References


Table 1: Boundary and triple junction statistics for the EM and CP samples. Columns 3 through 6 represent the percentage of boundaries classified as $\Sigma 3$, $\Sigma 9$, or $\Sigma 27$ in each of the 2 samples through multiple measured annealing states. Special boundaries fraction, $f_{\Sigma}$, is the fraction of all boundaries with $f_{\Sigma \leq 27}$. Columns 7 through 10 represent the percentage of triple junctions classified as $J_0$, $J_1$, $J_2$, or $J_3$.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Anneal</th>
<th>$f_{\Sigma 3}$</th>
<th>$f_{\Sigma 9}$</th>
<th>$f_{\Sigma 27}$</th>
<th>$f_{\Sigma \leq 27}$</th>
<th>$J_0$</th>
<th>$J_1$</th>
<th>$J_2$</th>
<th>$J_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>EM</td>
<td>0</td>
<td>20.2</td>
<td>11.5</td>
<td>7.6</td>
<td>39.3</td>
<td>16.0</td>
<td>46.4</td>
<td>8.6</td>
<td>28.9</td>
</tr>
<tr>
<td>EM</td>
<td>1</td>
<td>24.2</td>
<td>11.2</td>
<td>7.0</td>
<td>42.4</td>
<td>13.4</td>
<td>50.8</td>
<td>7.0</td>
<td>28.9</td>
</tr>
<tr>
<td>EM</td>
<td>2</td>
<td>24.0</td>
<td>10.9</td>
<td>6.8</td>
<td>41.7</td>
<td>13.6</td>
<td>51.2</td>
<td>6.9</td>
<td>28.3</td>
</tr>
<tr>
<td>CP</td>
<td>0</td>
<td>15.3</td>
<td>5.7</td>
<td>3.4</td>
<td>24.3</td>
<td>37.1</td>
<td>50.2</td>
<td>2.8</td>
<td>10.0</td>
</tr>
<tr>
<td>CP</td>
<td>1</td>
<td>14.4</td>
<td>4.7</td>
<td>2.5</td>
<td>21.6</td>
<td>35.9</td>
<td>53.3</td>
<td>1.8</td>
<td>9.0</td>
</tr>
</tbody>
</table>

Table 2: Summary of the single largest and 5 largest TRDs found in the EM and CP samples at various annealing states.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Anneal</th>
<th>Longest TRD</th>
<th>5 Longest TRDs</th>
<th>Total grains in volume</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$N_g$</td>
<td>% total grains</td>
<td>% total volume</td>
</tr>
<tr>
<td>EM</td>
<td>0</td>
<td>1203</td>
<td>11.6</td>
<td>14.7</td>
</tr>
<tr>
<td>EM</td>
<td>1</td>
<td>1395</td>
<td>12.2</td>
<td>14.0</td>
</tr>
<tr>
<td>EM</td>
<td>2</td>
<td>1187</td>
<td>12.7</td>
<td>14.6</td>
</tr>
<tr>
<td>CP</td>
<td>0</td>
<td>54</td>
<td>0.1</td>
<td>0.3</td>
</tr>
<tr>
<td>CP</td>
<td>1</td>
<td>173</td>
<td>0.7</td>
<td>4.0</td>
</tr>
</tbody>
</table>

Table 3: Summary of the single largest and 5 largest TRDs found in the EM and CP samples at various annealing states using 2D sections individually.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Anneal</th>
<th>Longest TRD</th>
<th>5 Longest TRDs</th>
<th>Total grains in volume</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$N_g$</td>
<td>% total grains</td>
<td>% total area</td>
</tr>
<tr>
<td>EM</td>
<td>0</td>
<td>42 ± 11</td>
<td>6.2 ± 1.6</td>
<td>9.6 ± 3.1</td>
</tr>
<tr>
<td>EM</td>
<td>1</td>
<td>64 ± 14</td>
<td>7.0 ± 1.6</td>
<td>9.5 ± 3.5</td>
</tr>
<tr>
<td>EM</td>
<td>2</td>
<td>62 ± 14</td>
<td>7.3 ± 1.6</td>
<td>9.5 ± 3.3</td>
</tr>
<tr>
<td>CP</td>
<td>0</td>
<td>12 ± 2</td>
<td>0.5 ± 0.1</td>
<td>0.5 ± 0.3</td>
</tr>
<tr>
<td>CP</td>
<td>1</td>
<td>15 ± 5</td>
<td>1.3 ± 0.5</td>
<td>3.1 ± 2.4</td>
</tr>
</tbody>
</table>

Table 4: Average and maximum values of length of longest chain (LLC) and polysynthetism ($p$) for all TRDs identified in the two samples across various annealing states.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Anneal</th>
<th>$LLC_{\text{max}}$</th>
<th>$&lt;LLC&gt;$</th>
<th>$p_{\text{max}}$</th>
<th>$&lt;p&gt;$</th>
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</thead>
<tbody>
<tr>
<td>EM</td>
<td>0</td>
<td>23</td>
<td>3.90</td>
<td>3.58</td>
<td>1.37</td>
</tr>
<tr>
<td>EM</td>
<td>1</td>
<td>23</td>
<td>3.65</td>
<td>4.22</td>
<td>1.46</td>
</tr>
<tr>
<td>EM</td>
<td>2</td>
<td>22</td>
<td>3.56</td>
<td>4.10</td>
<td>1.44</td>
</tr>
<tr>
<td>CP</td>
<td>0</td>
<td>13</td>
<td>2.43</td>
<td>3.00</td>
<td>1.15</td>
</tr>
<tr>
<td>CP</td>
<td>1</td>
<td>12</td>
<td>2.39</td>
<td>5.20</td>
<td>1.18</td>
</tr>
</tbody>
</table>
Table 5: Summary of the single largest TRDs found in the EM and CP samples at various annealing states as a function of the cutoff value of $N$ in definition of TRD using up to $\Sigma^3$.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Anneal</th>
<th>Longest TRD $(N = 1)$</th>
<th>Longest TRD $(N = 2)$</th>
<th>Longest TRD $(N = 3)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>EM</td>
<td>0</td>
<td>1203</td>
<td>1264</td>
<td>1293</td>
</tr>
<tr>
<td>EM</td>
<td>1</td>
<td>1395</td>
<td>1465</td>
<td>1484</td>
</tr>
<tr>
<td>EM</td>
<td>2</td>
<td>1187</td>
<td>1238</td>
<td>1258</td>
</tr>
<tr>
<td>CP</td>
<td>0</td>
<td>54</td>
<td>75</td>
<td>78</td>
</tr>
<tr>
<td>CP</td>
<td>1</td>
<td>173</td>
<td>178</td>
<td>184</td>
</tr>
</tbody>
</table>
Figure 1: 3D visual for the (a) EM sample, and (b) CP sample prior to annealing. The grain size differences are visually apparent here.
Figure 2: 3D visual of the 5 largest TRDs ranked by number of connected grains in (a) EM sample, and (b) CP sample. Note the significant volume and size of the TRDs in the EM sample. The gray edges represent the physical extent to the cylindrical (wire) sample measured volume.
Figure 3: Fractal representation of the twinning tree for the largest TRD in the EM sample in the (a) Anneal 0 state, (b) Anneal 1 state, and (c) Anneal 2 state. The central box represents the central grain, and the number in each box is the number of grains found with that unique orientation. Each red line represents a specific $\Sigma 3$ variant. Each black line represents branches of the tree up to 8th generation which are not found in the microstructure. By visual inspection, the tree structure of the TRD remains almost completely intact throughout subsequent annealing.
Figure 4: Same cross-section of the grain boundary engineered samples measured through the stages of annealing. Each of the rows represents the same cross section for the sample at the initial state ((a)-(c)), after the first anneal ((d)-(f)), and after the second anneal ((g)-(i)). The three plots of the same cross section highlights the individual grain orientation ((a), (d), and (g)), identified TRDs ((b), (e), and (h)), and non-\(\Sigma^N\) boundary network ((c), (f), and (i)). All boundaries are plotted and colored in white for (a), (b), (d), (e), (g), and (h). Only non-\(\Sigma^N\) boundaries are shown in (c), (f), and (i).
Figure 5: An example of a TRD being fragmented into 4 distinct TRDs when considering only the available 2D data. Each column represents an individual horizontal cross-sectional slice of the EM material in the Anneal 0 state. The two cross-sections represented here are physically offset by 40µm along the cylinder axis. The first row represents the grain map with non-CSL boundaries white. The second row presents a TRD map with only TRD boundaries white when considering the 2D slice individually. The third row presents a TRD map with only TRD boundaries white when considering the full 3D data. White x’s denote a TRD of interest that is known to be spatially connected in a single cross-section but becomes fragmented at a higher cross-section position.
Figure 6: Threshold determination for $p_{\text{random}}$. Blue colored plots represent the cumulative frequency from the normalized histogrammed values of $p_{\text{random}}$ when comparing two TRDs in the volume against each other while the color differences correspond to varying level of $N$ as a cutoff value in the search. Nearly all pairs of TRDs that are uncorrelated produce a value of $p_{\text{random}} \geq 0.8$. The gray colored plots represent the cumulative frequency from the normalized histogrammed values of $p_{\text{random}}$ when a single TRD is split and compared against each other while the color differences correspond to varying level of $N$ as a cutoff value in the search. Nearly all pairs of TRDs that are correlated produce a value of $p_{\text{random}} \leq 0.8$. 
Figure 7: Size of the largest cluster in the EM, CP, and Voronoi microstructure when $f_\Sigma$ is varied randomly. Plots include standard error bars determined from the number of trials attempted.
Figure 8: Size of the largest $\Sigma^3$RD cluster in the EM sample when the simulated special boundary population is downsampled from only existing CSL boundaries to produce a simulated special fraction, $f_\Sigma$. $f_\Sigma$ is varied up to and above the measured special fraction in the CP sample. Plots include standard error bars determined from the number of trials attempted.