Percolation Paths of Three-Dimensions in Sensitized Stainless Steel

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PERCOLATION PATHS OF THREE-DIMENSIONS
IN SENSITIZED STAINLESS STEEL

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GRADUATE COMMITTEE APPROVAL

This dissertation has been read by each member of the following graduate committee and by majority vote has been found to be satisfactory.

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ABSTRACT

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Doctor of Philosophy

The study of three-dimensional percolation paths through materials is important in its contribution to understanding defect sensitive properties of materials. This work shows the importance of grain boundary character in modeling defect sensitive boundaries. Also presented are trends of percolation of sensitized grain boundaries in 304 stainless steel (304SS). Of particular interest is how open paths form in a three-dimensional model created through serial sectioning. Evidence is presented that triple or quadruple points that contain typically two boundaries with special character that intersect the percolation path break up the path. Some boundaries with no known special qualities; they are not CSL or low angle boundaries, resist corrosion.
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suggestions he took it upon himself to do so. Many of the critical decisions as to the
direction of my research were influenced by him (including the decision to move ahead
rather than start all over a mere six months from the end). My daughter, Kylee, also
deserves gratitude for playing by my side at the computer and allowing me to finish this
work. I do not think she minded the few extra movies she was allowed to watch. I hope
to be able to help her achieve her goals as so many others have helped me to achieve
mine.
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1 INTRODUCTION

The presence of certain types of grain boundaries in polycrystalline materials affects material properties [1-5]. Certain of these properties are defect sensitive properties such as the sensitization of 304 stainless steel (304SS) [6-8]. Materials with defect sensitive properties are susceptible to the formation of connected clusters of defects along grain boundaries.

Percolation is the formation of clusters, or connected points through a two-dimensional or three-dimensional structure that allows an uncut line or surface to form from point to point through a network of points. For example, if a porous stone is immersed in water, the center of the stone gets wet only if connected paths exist from the surface of the stone to the center (Figure 1.1). Likewise, connected paths of defect sensitive grain boundaries exist in 304SS from the edge of the sample inward. If a sensitized sample of 304SS is placed in a corrosive environment, the connected paths of sensitized grain boundaries allow corrosion to propagate inward along the grain boundaries (Figure 1.2). This is of particular interest if the corrosion path reaches the critical crack length for the material. If corrosion resistant boundaries are encountered, travel along the pathway is effectively blocked, thereby producing a critical percentage of sensitized boundaries, or percolation threshold $p_c$, below which a connected path through the entire system does not exist [9].
This dissertation shows how percolation paths form on the surface of 304SS and how these paths might form from the surface inward in a three dimensional model. The location and crystal orientation of points used for determining percolation behavior were obtained using a combination of serial section techniques and electron backscatter diffraction patterns gathered and analyzed with Orientation Imaging Microscopy (OIM) [10]. The character of certain grain boundaries affects sensitization and hence percolation; care must be taken to categorize a grain boundary as special, or resistant to corrosion for use in determining percolation trends. Some extrapolation of two dimensional data into three dimensions is accomplished using trace analysis methods [11-13] as well as serial sectioning.
Figure 1.2: The white boundaries are those predicted to sensitize in a 304SS sample. In the image on the left, the path is broken within the circle and corrosion cannot follow from the right hand edge inward. In the image on the right the pathway is unbroken thereby allowing corrosion to progress.
2 BACKGROUND

2.1 Sensitization of Stainless Steel

Sensitization of Austenitic 304 stainless steel occurs at temperatures between 425 and 815 °C when chromium carbides \((\text{Fe,Cr})_{23}\text{C}_6\) precipitate at grain boundaries. The chromium carbide precipitates are very high in chromium content, whereas the matrix alloy is depleted of chromium near the grain boundaries. The chromium depleted area is much less resistant to corrosion than the surrounding grains [14]. Hence sensitization is a good phenomenon to model percolation behavior because of its localization along grain boundaries and its preference for specific grain boundary types. The occurrence of precipitates increases when the misorientation angle of the boundary plane increases [15], and studies have found that the susceptibility to sensitization is linked to the grain boundary character [12, 15].

Grain boundary character is fully defined by five macroscopic and three microscopic parameters [16]. Two macroscopic parameters are needed to describe the orientation of the boundary plane normal and three describe the misorientation. Four of the five macroscopic parameters can be determined from two-dimensional data. The inclination of the boundary is not recoverable from two-dimensional data, only the trace of the boundary can be recovered (Figure 2.1). This trace can be used to determine the likelihood that the boundary plane is a particular plane, and can also definitively calculate
which crystallographic planes a boundary cannot have [11-13]. The three microscopic parameters are not normally addressed by these experimental methods and are not considered further here.

The two classifications of boundaries found to be most resistant to corrosion are coherent $\Sigma 3$ boundaries and boundaries with a low angle (less than 15 degrees) of misorientation between adjacent grains. Some high angle boundaries with no currently distinguishing character have also been noted to resist corrosion. It is believed that the boundary plane of these high angle grain boundaries might contain a lower energy boundary but the low occurrence of such boundaries has not yet led to a statistical analysis of this phenomenon [12].

![Figure 2.1: a) shows the trace of the boundary on the surface. The addition of angle b) fully defines the inclination of the boundary.](image)

2.2 Percolation

The study of percolation of grain boundaries through materials has been deemed important because the spatial arrangement of grain boundaries, as well as the statistical presence of certain special boundaries, has been found to be of significance in the resistance to intergranular degradation [17-24]. Sensitized stainless steel that has
connected paths of sensitized grain boundaries may reach the percolation threshold $p_c$, or other critical dimensions such as the critical crack length for the material under prescribed loading conditions.

Wells et al. [17] have shown two additional statistically important thresholds. The first threshold is seen when 23% or below of the total grain boundaries are sensitized. When below this threshold ductile fracture of test specimens resulted, suggesting that sensitized paths of grains did not form long enough paths for stress corrosion cracking to affect the failure of the material. When the total percentage of sensitized grain boundaries was at 89% or above, the second percolation threshold was reached. This resulted in complete brittle intergranular failure of test specimens. Test specimens with percentages of sensitized grains between these two thresholds showed a mixture of transgranular and intergranular failure. Wells’ results agreed with computer percolation simulations based on equi-axed grains formed of Kelvin’s tetrakaidecahedron [25]. Wells performed coarse serial sectioning to ensure that trends were seen on more than one surface.

Gaudett and Scully [18, 19] have shown that the determination of which boundaries are active is not only subject to an assessment of whether the boundary is sensitized or not but also on the minimum Cr content associated with the depleted boundary. This means that some boundaries are more depleted than others and are more susceptible to crack propagation. For 304SS with a bulk Cr concentration of 18.5%, variations in Cr content from 10 to 15 weight% have been measured at individual grain boundaries. Boundaries with lower Cr concentrations are more susceptible to crack growth. The critical concentration of Cr at the grain boundary varies from corrosion environment to corrosion environment. In a very corrosive environment it is supposed
that the level of sensitization is less important than the percolation threshold or percentage of sensitized boundaries present. However, for less corrosive environments the determination of how many boundaries are sensitized may not be enough information to determine percolation behavior. There is a correlation between grain boundary character and the severity of Cr depletion along the boundary [12, 20]. This is seen when the coherent portion of twins in fcc materials do not corrode or wet along the boundary but the non-coherent portion does.

Schuh et al [24] have developed a method to analyze the structure and topology of two-dimensional grain boundary clusters and have used it to characterize topological changes brought about by grain boundary engineering Inconel 600.

Most information regarding percolation and grain boundary behavior has been gathered either in two dimensions or by computer simulation, and little has been studied on the contribution of the inclination of special types of boundaries and their contribution to improved properties. From data that does include the inclination of the boundary, it is difficult to amass enough information to provide a statistical analysis. Also, the statistical importance of percolation, or linked travel, of special types of boundaries (i.e., sensitized or unsensitized boundaries) and the presence of certain grain boundary types (i.e., coherent twins) has not been received significant attention from researchers.

The ease of which boundaries allow carbides to form is believed to be directly linked to the grain boundary character, which includes both misorientation and the inclination of the boundary. It has been shown that percolation behavior of stress corrosion cracking in 304SS has important thresholds at certain statistical presence of sensitized boundaries. If the percentage of beneficial grain boundary orientations or the
percolation thresholds can be altered, small changes in crystal orientation can make large changes in the behavior of the material. This will be especially beneficial if changes can be made around percolation thresholds.
3 EXPERIMENTAL PROCEDURE

3.1 Sample Preparation

All experiments for this research used a 0.635 cm (1/4 inch) thick sample of hot rolled 304SS with the constituents shown in Table 3.1. A solution soak was undergone at 982.2 °C (1800 °F) for 23.5 hours in a vacuum furnace, where the sample was enclosed with titanium sponge in stainless steel foil. The long solution soak was used to grow the average size of the grains so that higher resolution data could be obtained. The sample was then cut by wire EDM into six rectangular samples and one 1.27 cm (1/2 inch) diameter cylindrical sample (to facilitate polishing and to retain a parallel surface). The first series of rectangular samples were then sensitized at 675 °C under the same conditions as above between 2-20 hours to obtain a variety of sensitization levels. The samples were lapped parallel on all six sides and three adjacent sides were polished with colloidal silica. OIM data were taken in the one corner where the polished sides meet (Figure 3.1).

The samples were etched with 10% oxylic acid at 0.35 A for 30 seconds [26] and SEM images were obtained after each etch that clearly outlined grain boundaries sensitive to corrosion (Figure 3.2 through Figure 3.3). (An initial attempt was made to simultaneously obtain misorientation and chromium concentration at the boundary using EDS x-ray microanalysis and OIM. However, since the interaction volume of x-rays is
large compared to the thickness of the chromium depleted region, the results were not satisfactory in determining where chromium depleted regions existed). There were no observable corroded boundaries at the 2-hour heat treat. Only fully defined boundaries were considered in the following statistical analyses; boundaries containing pitting only were not considered. This light etch was chosen rather than a harsh, longer etch to make it possible to note differences between lightly and heavily sensitized boundaries. The rectangular samples shown in Figure 3.1 were used to observe percolation trends on the surface of the sample and for trace analysis. This is discussed in more detail later in Section 3.3

Table 3.1: Constituents of 304SS

<table>
<thead>
<tr>
<th>C</th>
<th>Mn</th>
<th>P</th>
<th>S</th>
<th>Si</th>
<th>Ni</th>
<th>Cr</th>
<th>Mo</th>
<th>Cu</th>
<th>N</th>
<th>Co</th>
<th>Nb</th>
</tr>
</thead>
<tbody>
<tr>
<td>.0510</td>
<td>1.150</td>
<td>.0300</td>
<td>.0010</td>
<td>.4500</td>
<td>8.1300</td>
<td>18.2600</td>
<td>.4000</td>
<td>.3500</td>
<td>.0650</td>
<td>.1500</td>
<td>.0000</td>
</tr>
</tbody>
</table>

3.2 Serial Sectioning

The 1.27 cm diameter sample was sensitized at 675 °C for 8 hours under the same conditions as above. The sample was then lapped flat on both ends to within 3 μm to ensure that the surfaces were parallel. One side was then polished with colloidal silica using a Logitech PM5 lapping and polishing machine. Microhardness indents were placed in the center of the sample at the four corners of the area of interest (2000 μm x 2000 μm). One indent was offset to facilitate aligning the sample (Figure 3.5). After polishing, an OIM scan was obtained in a square grid pattern with a 5 μm step size, shown in Figure 3.6. The sample was then re-polished for approximately 5 hours at 20
rpm with a predetermined load to remove approximately 5 µm of material. Microhardness indents were then reapplied and the process was repeated to obtain 41 sections with approximately 260 µm total thickness.

After each polish, the microhardness indents were remeasured and new indents were applied over the old ones and measured for the new layer (Figure 3.7). The removal process was difficult to regulate and progressed nonlinearly with time. For the same polishing time, removal rates were approximately 2.5-8 µm. The depth of the microhardness indents before and after polishing was used to determine the thickness removed for each layer.

The microhardness indents were used to align each sample under the SEM to obtain OIM images. Occasionally the indenter’s position calibration would change and the indents would not align correctly (Figure 3.8). This resulted in errors in the alignment of the images. To correct this, triple junctions at the bases of stable twin features in the microstructure were used (Figure 3.9). The locations of these twins were mapped through the thickness of the sample. Since the edges of most twin features follow parallel paths, the change in position of these triple junctions from one layer to another should be small and should follow a pattern.

For example, some points should shift left and other should shift right. Triple junction locations were chosen to distribute the shift trends of the sampled triple junction points. The vertical and horizontal shifts were recorded for each triple junction on each successive layer. Then $x$, $y$ and rotational shifts were calculated using an optimization routine that minimized the difference in the locations of the triple junction between one layer and the layer above. A transformation was performed on each layer to add the $x$, $y$
and rotational shift. This method gave an improvement over alignment using the microhardness indents as shown in Figure 3.10. (Since gathering this data set, more advanced ideas for accurate serial sectioning have been put forth [27].) Similar serial sectioning methods have been used by Randle [24] to obtain information about the inclination of boundaries.

Figure 3.1: 3-D OIM cube with 4 hour sensitization sample.
Figure 3.2: SEM image of etched boundaries for 4 hour sensitized sample (20x).

Figure 3.3: SEM image of etched boundaries for 4 hour sensitized sample (10x).
Figure 3.4: OIM image of all boundaries and grains for 4 hour sensitized sample. Grey scale shading represents image quality.

Figure 3.5: Microhardness indents to track location of the scans through serial sectioning.
Figure 3.6: OIM map of one serial section. Color represents orientation according to the inverse pole figure.
Figure 3.7: Two microhardness indents placed over the top of each other. In this instance, there is good alignment between the two layers.

Figure 3.8: Two microhardness indents placed over the top of each other. In this instance, there is poor alignment between the two layers. Several misalignments cause drift in the placement of the indents and make them a poor choice for aligning the serial sections.
Figure 3.9: Twin triple-junctions were used to align the serial sections. The figure shows a sample of the triple-junctions used.
3.3 Modeling the Sensitized Boundaries

Percolation clusters were modeled in both two and three dimensions. First, OIM maps of all surface boundaries and correlating maps of surface sensitized boundaries were obtained (Figure 3.11 and Figure 3.12). These maps were used to create a model of boundaries with specific character that were susceptible to corrosion. Low angle boundaries (less than 15° misorientation across the boundary) and coincident-site lattice (CSL) orientations of $\Sigma 3$ are considered to be resistant to corrosion (where the more restrictive geometric criterion given by Palumbo [28] is used). An example of the results can be seen in Figure 3.13. This assumption is consistent with what has been seen by Randle and Gertsman and Bruemmer [12, 20] with the exception that only coherent $\Sigma 3$ boundaries are seen to always resist corrosion. By comparing this predicted pattern of
corrosion with boundaries that in actuality did corrode, this model proves to be fairly accurate (Figure 3.13 through Figure 3.16) with the following discrepancies:

- Pitting of some $\Sigma 1$ boundaries
- Corrosion of incoherent $\Sigma 3$ boundaries
- Some higher $\Sigma$ boundaries (particularly $\Sigma 5$, $\Sigma 9$, and $\Sigma 11$) did not corrode
- A small percentage of other “non-special” boundaries also did not corrode.

Low angle boundaries that pitted had misorientation angles in the 14-15° range. Bennett and Pickering [29] have also seen boundaries in this range exhibit non-special behavior for austenitic stainless steels, and a more restrictive definition of low angle boundary would be useful to correct this problem. It is important to note that the default resolution of OIM for boundary recognition is 1°.

Corrosion of some of the $\Sigma 3$ boundaries is explained by the following. CSL boundaries have a given fraction of atoms in the grain boundary plane that are coincident to both lattices across the grain boundary. The $\Sigma$ value denotes the fraction of atoms in coincidence (e.g., $\Sigma 3$ defines 1 out of 3 atoms between two adjacent lattices to be coincident at the boundary). A CSL designation however, tells nothing about the inclination parameter of the boundary [30].

For example, recrystallization twins in fcc materials can be characterized as a 60° rotation about a $<111>$ crystal direction, and have a $\Sigma 3$ relationship. A $\Sigma 3$ boundary should be a special, low energy or coherent boundary if the 111/111 planes of the two adjacent grains coincide along the boundary plane (Figure 3.17). There are only certain
traces of the boundary plane in two-dimensional scans that indicate the plane might lie on the \{111\} plane. Randle and co-workers have worked extensively with EBSD (electron back-scatter diffraction) in identifying and studying twin boundaries. Using trace analysis [17,18,31,32], predictions can be made concerning which boundaries might have an inclination angle that would result in this special relationship. Serial sectioning, or some other method to accurately assess the inclination of the boundary, is required to truly define a coherent boundary, however Randall in one study has shown through serial sectioning that 90% of boundaries satisfying the two-dimensional twin criterion also met the criterion in three dimensions [13].

Figure 3.11: OIM map of all grain boundaries in 4 hour sensitized sample, face 1. 1500 x 1500 \(\mu m\).
Figure 3.12: This is a representation of all boundaries that sensitized on the surface of the 4-hour sensitized sample. Boundaries that connect form two-dimensional percolation clusters.

Figure 3.13: Predicted percolation clusters assuming $\Sigma_1$ and $\Sigma_3$ boundaries did not sensitize.
Figure 3.14: Observed percolation clusters without including the sensitized $\Sigma 1$ or $\Sigma 3$ boundaries.

Figure 3.15: All $\Sigma 3$ boundaries.
Figure 3.16: $\Sigma 3$ boundaries that sensitized. Note the isolation of the short, incoherent boundaries. They characteristically only connect to coherent $\Sigma 3$ boundaries.
Figure 3.17: Figures a) and b) show the arrangement of the center of the atoms of a face-centered cubic structure. Figure c) shows a \{111\} plane and d) shows the extension of that plane. Figure e) shows a second \{111\} plane superimposed onto of the first, this relationship is only a $\Sigma 6$ relationship.

Table 3.2: A breakdown of the percentages of specific types of boundaries seen. Most $\Sigma 3$ boundaries were resistant to sensitization. Almost all $\Sigma 9$ boundaries sensitized.

Grain size was calculated by ignoring twin boundaries.

<table>
<thead>
<tr>
<th>Heat treat (hrs)</th>
<th>Grain size (µm)</th>
<th>% $\Sigma 3$ boundaries</th>
<th>% unsensitized $\Sigma 3$ boundaries</th>
<th>% $\Sigma 9$ boundaries</th>
<th>% unsensitized $\Sigma 9$ boundaries</th>
<th>% low angle boundaries</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>316</td>
<td>58</td>
<td>54</td>
<td>7</td>
<td>2.2</td>
<td>2.6</td>
</tr>
<tr>
<td>8</td>
<td>402</td>
<td>60</td>
<td>52</td>
<td>5</td>
<td>0.6</td>
<td>5.1</td>
</tr>
<tr>
<td>10</td>
<td>459</td>
<td>62</td>
<td>51</td>
<td>5</td>
<td>0.3</td>
<td>9.5</td>
</tr>
<tr>
<td>20</td>
<td>531</td>
<td>59</td>
<td>52</td>
<td>6</td>
<td>1.1</td>
<td>5.2</td>
</tr>
</tbody>
</table>
A CSL designation of $\Sigma 3$ is not enough to indicate a low energy or corrosion resistant boundary. Only coherent $\Sigma 3$ boundaries are seen to be resistant to corrosion. Here about 13% of the $\Sigma 3$ boundaries sensitized (Table 3.2). However, in 304SS $\Sigma 3$ boundaries are typically twins, and the incoherent portions of the twin do not normally connect to other grains but are isolated in the center of a grain or connect to coherent $\Sigma 3$ boundary sections (Figure 3.15). Therefore for percolation studies, neglecting the difference between coherent and incoherent $\Sigma 3$ boundaries does not affect the connectivity of percolation paths. This can been seen by comparing all $\Sigma 3$ boundaries and $\Sigma 3$ boundaries that were seen to sensitize (Figure 3.15 and Figure 3.16). Note the many small sections at the ends of twins and their isolation from any other grain boundary. In three dimensions, as these twins grow to match another grain, the boundary relationship changes and is no longer a $\Sigma 3$ boundary (Figure 3.18). However, incoherent $\Sigma 3$ boundaries do contribute to the overall mass of the system and change the approach.
needed to deal with systems of this type from a traditional mathematical percolation model.

$\Sigma 9$ boundaries were also examined, and approximately 16% of them were seen to resist corrosion. This could be due to the fact that only a light etch was used. A few other higher $\Sigma$ boundaries such as $\Sigma 5$ and $\Sigma 11$ were also seen to resist corrosion.

The appearance of non-special boundaries (boundaries that do not have small misorientation angles or a CSL relationship) that are resistant to corrosion is provocative. These boundaries may coincide with the observation that if even one of the interface planes is near a low energy plane, then the entire boundary can be of relatively low energy and hence, resistant to sensitization [19]. These boundaries were examined to see if they might be boundaries with a low-index crystallographic plane on one side of the boundary. Work performed by Saylor and co-workers [33] states that the plane with minimum energy in magnesia is the $\{100\}$ plane. These boundaries are not CSL boundaries but are expected to have low energy by using the theory proposed by Wolf [34], that the grain boundary energy is the sum of the two surface energies that make up the boundary, minus a binding energy.

In one 1500 x 1500 µm scan, 14 specific, individual boundaries resisted corrosion and possess no apparent ‘special’ properties. They were examined using trace analysis techniques to determine if they might lie along a low index crystallographic plane. Low index planes with the best match included $\{100\}$, $\{210\}$, $\{310\}$ and $\{410\}$ planes. However trace analysis showed that only two of the 14 boundaries could possibly lie along the above low-index planes. These non-special boundaries merit further study. Some of the corrosion resistant boundaries that did not have low index planes were
boundaries with high curvature. These boundaries were often located away from triple junctions.
4 RESULTS AND DISCUSSION

4.1 Percolation Statistics in Two Dimensions

An investigation of percolation statistics in two dimensions was used to validate the assumptions of which boundaries sensitize for use in three dimensions. Percolation clusters and other percolation statistics were determined from a square grid of points spaced 5 µm apart, whose (x, y) coordinates were recovered from the OIM raw data sets. Whether the point is sensitized and hence included in the cluster or not was determined by either visual confirmation in optical micrographs or by using the model for sensitization discussed in the above section. Percolation clusters of sensitized boundaries are looked at in this study.

A sample of data obtained is shown in Figure 3.11 through Figure 3.16. Additional data not shown here can be found in the Appendix. Two-dimensional optical and OIM images from three sides of square samples sensitized at 2, 4, 8, 10, and 20 hours were obtained. Optical and OIM images were also obtained for 42 serial sections from an 8 hour heat treated sample. The two-dimensional data is used to produce a model for looking at the recreated three-dimensional, serial-sectioned data. The surfaces of the serial sections were not etched as this caused difficulty in the serial-sectioning process. Therefore each boundary in the recreated three-dimensional model could not be labeled sensitized or not-sensitized by optical observation of corrosion at the boundary. A
comparison of percolation statistics between boundaries optically observed to corrode and boundaries assumed to corrode on the two-dimensional surfaces was used to validate assumptions of which boundaries sensitize for use in creating a three-dimensional model of percolation.

Correlation length $\varsigma$ is defined as the average distance between two points belonging to the same cluster [35]. The correlation length is the radius of those sites which give the main contribution to the mean cluster size distribution near the percolation threshold. It can be defined as:

$$\varsigma^2 = \frac{2\sum_{i=1}^{N} (R_g^2) M_i w_i}{\sum_{i=1}^{N} M_i w_i}$$

(4.1)

where $N$ is the total number of clusters in the data set and:

$$w_i = \frac{M_i}{M^*}$$

(4.2)

where $M_i$ is the mass$^1$ of the $i^{th}$ cluster and $M^*$ is the total mass of the microstructure. Mass is equivalent to boundary length in two-dimensions or boundary area in three dimensions. It is measured in $\mu$m or $\mu$m$^2$. The radius of gyration $R_g$ is analogous to a two dimensional cluster rotated around an axis through its centre of mass and

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$^1$ Mass used in the context of percolation notation refers to percolation bond length or area. It does not refer to mass as measured in kg. It is a term peculiar and particular to the field of percolation study.
perpendicular to the cluster. The kinetic energy and angular momentum of this rotation is the same as if all points were on a ring of radius $R$ centered about the axis [9]. This is represented by:

$$R^2_g = \sum_{i=1}^{s} \frac{\left| r_i - r_o \right|^2}{s}$$  \hspace{1cm} (4.3)

$$r_o = \sum_{i=1}^{s} \frac{r_i}{s}$$  \hspace{1cm} (4.4)

where $s$ is the number of active bonds in the cluster and $r$ is the position of the $i^{th}$ bond in the cluster. A bond is the connection between two active points. The center of mass is set to be at the 0 coordinate for each cluster.

A comparison of the percolation statistics from the predicted corroded boundaries (Figure 3.13) and observed corroded boundaries (Figure 3.14) for two dimensions is given in Table 4.1. The largest differences between the two data sets occur because the incoherent $\Sigma 3$ boundaries sensitize. The contribution of these sensitized boundaries can be seen in a comparison of the observed corroded boundaries (Figure 3.12) and the same area with $\Sigma 3$ boundaries removed (Figure 3.13).

This model of which boundaries sensitize is conservative in its prediction of the longest path and average cluster size, over-predicting the mass of them both. These are two of the most important percolation measurements along with the percolation threshold (which is difficult to measure in this set of materials since all samples examined exceeded the percolation threshold). For example, as discussed by Gertsman and Tangri [21], just
one crack may be enough for a crucial component to fail owing to intergranular degradation. There is a high risk of failure even if 99 out of 100 percolation paths are small and 1 is above a critical size. The average cluster mass is important because as the percolation threshold $p_c$, is approached the average cluster size increases.

An automated trace-analysis process was attempted to determine which of the $\Sigma 3$ boundaries were coherent. Trace analysis in this case resulted in poor resolution since most of the $\Sigma 3$ boundaries are small in length for the step sized used in gathering this data (many were less than 25 µm or 5 steps in length). The automated approach was found to have varying results. Looking at the boundaries one at a time and hand picking parameters resulted in better consistency. This comparative analysis showed that coherent $\Sigma 3$ boundaries did not corrode and that incoherent $\Sigma 3$ boundaries did corrode. This type of comparison is time consuming and since the overall connectivity appears to be unaffected, whether a boundary is coherent or incoherent (see Section 3.3), this analysis was not done at this time. However, a comparison was made between the boundaries predicted to corrode, assuming that all $\Sigma 3$ boundaries are resistant to corrosion (Predicted), and what was seen on the two-dimensional surfaces (Observed), as shown in Table 4.1.

The presence of non-special boundaries that did not corrode, as discussed in the previous section, also affects the percolation statistics since these boundaries break up percolation clusters. The average cluster mass is 253 µm for the predicted data as compared to 83 µm for the observed paths. These non-special boundaries also account for the difference in the longest path. The longest path is predicted by the model to be 2385 µm but only appears as 1773 µm in the observed data set. The average

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length/diameter measurements show a prediction for more circuitous paths; the observed paths have a more direct line in nature.

Although differences between boundaries predicted to sensitize and those observed to sensitize are recognized, along with their contribution to variances in the percolation statistics of the 304SS, the model of sensitized boundaries is conservative in many aspects, such as predicting the longest path and average cluster size, and is used to look at percolation paths in three-dimensions.

In summary, a model of sensitized boundaries included all low angle boundaries below 15° and all \( \Sigma 3 \) boundaries. This is sufficient for initially defining percolation paths through the material. There is evidence that there are other boundaries resistant to sensitization and that higher \( \Sigma \) boundaries might also resist corrosion in low corrosive environments. This model was used to look at percolation statistics in two-dimensions and to build a three-dimensional model of connected sensitized boundaries.

*Table 4.1: Percolation statistics gathered from 2-D data sets in Figures 3.13 and 3.14.*

<table>
<thead>
<tr>
<th></th>
<th>Predicted</th>
<th>Observed</th>
</tr>
</thead>
<tbody>
<tr>
<td>Number of Clusters</td>
<td>( N )</td>
<td>49</td>
</tr>
<tr>
<td>Total Mass</td>
<td>( M^* )</td>
<td>6333 um</td>
</tr>
<tr>
<td>Avg. Cluster Mass</td>
<td>( M_{avg} )</td>
<td>253 um</td>
</tr>
<tr>
<td>Longest Path</td>
<td>( L )</td>
<td>2385 um</td>
</tr>
<tr>
<td>Avg. Length/Diameter</td>
<td></td>
<td>1.49</td>
</tr>
<tr>
<td>Correlation Length</td>
<td>( \varsigma )</td>
<td>5.17E+04</td>
</tr>
</tbody>
</table>
4.2 Observed Phenomena in Three Dimensions

A three-dimensional reconstruction of approximately 80 separate grains was created using IMOD, a three-dimensional graphics package developed at the University of Colorado, Boulder [36] (Figure 4.1). (All 42 layers are shown in the Appendix). Some interesting phenomena were observed. The first is the interconnectivity of two grains through each other. In many cases, instead of two grains being spherical in nature they interconnect with fingers going through each other as seen in Figure 4.2. Another interesting feature is the alignment of twins to each other in different grains. Second is the alignment of twins on a similar plane. In Figure 4.3, three twins are shown that align directly with each other at some point. Shown specifically here, the two large twins directly align in the bottom plane. The twins are unconnected at other points. This means that the alignment of all three twins could not be seen in a two-dimensional image. These images serve as examples of phenomena seen in three dimensions that are not readily apparent in two dimensions. As more complex models of materials are built to test theories and make predictions, it is important that these models be built as accurately as possible. Obtaining accurate three-dimensional data sets can act as guides for those making these models.
Figure 4.1: A three-dimensional representation of 80 grains in the serial sectioned 304SS. Views a, b and c show the same grains from different perspectives. In this instance, twins are counted and shown as individual grains.
Figure 4.2: Two grains, the upper with a twin, shown first separate and then melding together.

Figure 4.3: The alignment of three twins: The alignment of the upper light green twin along the same axis as the lower yellow twin can be seen on the bottom plane. The third pink twin has the same alignment of its long axis as the other two and melds into the lower yellow twin.

4.3 Percolation Statistics in Three Dimensions

By using the same model to predict boundaries that will sensitize, a three dimensional percolation cluster was reconstructed using IMOD. Assuming that the
initiation point for the cluster is a surface point, the cluster begins with one generation of connectivity. A generation of sensitized boundaries includes all boundaries that connect off of the previous generation. A single initiation point was identified as generation zero. All boundaries that connect to the initiation point are considered to be generation one. Then, consecutively, all boundaries that connect to a generation one boundary are considered to be generation two. A time progression visualization of the sequence of generations is shown in Figure 4.4. All points in the cluster that are surface points are equivalent initiation points for the cluster. General trends in percolation were observed from this reconstruction.

Figure 4.4: This shows the 3-D percolation cluster beginning from the surface of the sample. All boundaries are initially connected through the first generation shown in a). Figure b) shows the fifth generation with more boundaries added through localized connections through the third dimension. Figures c) and d) show generations 12 and 24. Figure e) shows the full percolation cluster at generation 52.

In the sample used for this analysis, the level of percolation is above the percolation threshold $p_c$. One cluster extends completely from edge to edge in the sample. This provides an open pathway for corrosion to follow. Locations in the interior of the material will not spontaneously corrode even if they are sensitized; they first need to be exposed to a corrosive environment. An open percolation pathway to the interior
provides this exposure. Identifying general trends of how open paths of sensitized boundaries form may lead to methods that block open paths.

There are areas where progression of the cluster is blocked by small areas called percolation voids. Here percolation voids are a single grain. Percolation voids are located at triple junctions or quadruple points that intersect the open pathway of the percolation cluster where typically two, but possibly one, of the branches are resistant to sensitization. It takes several generations before the void is encircled by sensitized boundaries. At the edges of these voids, bridges between two smaller clusters form and the size of the main cluster is greatly increased. Two sections with different z values are shown in Figure 4.5s and Figure 4.6. The first figure has two percolation voids marked a and b. Traveling through the material in the z direction, the two voids end and bridges form. An example showing boundaries only can be seen in Figure 4.7 and Figure 4.8.

The cluster increasingly grows in size through each successive generation, as shown in Figure 4.9. When edge effects are encountered the growth slows. The rate of growth decreases with each generation with occasional upward spikes (Figure 4.10). These spikes can indicate locations where percolation bridges occur connecting two smaller clusters together. The first spike in Figure 4.10 occurs when the percolation void b in Figure 4.5 and Figure 4.6 is surrounded and a smaller percolation cluster is joined to the main cluster.
Figure 4.5: Special boundaries are shown in white. Percolation voids a) and b) occur at triple junctions where two branches are resistant to corrosion.

Figure 4.6: At a different location in the z direction, the locations of the special boundaries have drifted and the triple junctions no longer contain two resistant branches. This allows two smaller percolation clusters to connect.
Figure 4.7: Here the connectivity is broken and a corrosion path is not formed at this point.

Figure 4.8: A few layers further, and a percolation bridge has formed, allowing a corrosion path to develop.
Figure 4.9: Growth of the percolation cluster shown per generation and measured in mass $M^*$ in µm.

Figure 4.10: Rate of change of total mass per generation. Upward spikes represent locations where percolation bridges form and group smaller clusters into the larger cluster.
Grain boundary engineered materials are often classified by the percentage of special boundaries present; typically $\Sigma 3$ boundaries are used for this classification. This material showed 60% $\Sigma 3$ boundaries and 52% corrosion resistant $\Sigma 3$ boundaries as shown in Table 3.2. In this sample, the percolation voids contained small grains on the order of 20-100 µm, well below the average grain size. This means that paths were found around the voids in a few generations and percolation could continue in the third dimension even though the percentage of special boundaries was fairly high at about 60%.

4.4 Comments and Suggestions for Future Work

If corrosion begins at the surface, progression of the damage front is dependent upon the length of the percolation paths and time. Any addition of length to the percolation path that does not penetrate deeper into the sample is advantageous. Paths that double back upon themselves are beneficiary. A percolation void delays the advancement of corrosion since more generations are required to move the corrosion front the same distance through the material. The density of percolation voids and their location in relationship with one another can control the rate of damage.

Percolation voids are defined as an entire grain located next to a triple junction or quadruple point where typically two, but possibly one, of the branches traveling along the grain are resistant to sensitization. Other locations on the grain may or may not resist corrosion. This results in a pseudo-genus development where the entire grain defines the location of the percolation void but the void is not a closed loop. Progression around the void adds length to the percolation path without expanding the damage front into the material.
Future work could be done to clarify the effect of percolation voids on damage propagation. These types of voids may be a result of the particular processes the material experienced and variations in the formation of voids may exist. The addition of EPR testing would greatly aid in correlating with already published work in two-dimensions and coarse serial sectioned experiments.

EPR testing of each serial section would also validate the existence of corrosion resistant ‘non-special’ boundaries referred to in Section 3.3. With high resolution EBSD or TEM analysis the full definition and/or curvature of these non-special boundaries could be looked at. Since small changes in areas resistant to corrosion can have significant effect on the progression of damage, the addition of such boundaries could have a large affect on material properties. It is my recommendation that this is an area that requires further observation.

Also of interest is how the addition of twins aid in breaking up percolation paths. Since it is the percentage of coherent $\Sigma 3$ boundaries and not the percentage of all $\Sigma 3$ boundaries present in a material that appears to change the material behavior the ability to track the difference is significant.
5 CONCLUSIONS

1. The presented model, that all low angle and Σ3 boundaries are resistant to sensitization, gives a conservative model of the statistics of percolation clusters in that it over predicts the longest path and average cluster size.

2. Some non-special boundaries resist sensitization. These few boundaries can greatly change the percolation statistics and were often located away from triple junctions. An increased number of these boundaries could greatly improve percolative phenomena.

3. The model created from serial sections allows phenomena to be seen that would be missed in two-dimensions only. Very few three-dimensional data sets have been obtained with this many serial sections. The existence of the three-dimensional information by itself is very valuable in its contribution to modeling true microstructures.

4. Great care should be taken when characterizing CSL boundaries as special. A CSL identification alone is not enough to classify a boundary. The inclination of the boundary plays an important role in the behavior of the boundary.

5. Even though the percentage of special boundaries was about 60%, this sample was still above the percolation threshold $p_c$.

6. Percolation voids can occur at quadruple points or triple junctions where one or more boundary is special. Observed percolation voids were small, and bridges between
clusters form at their edges causing the size of the main percolation cluster to increase.

7. Here, sensitization was used, but the same model might be applicable to other percolative-type phenomena such as intergranular cracking.

Note: For the full color 3-D model with generation progression of the boundaries, or the full 3-D data set with x,y,z and orientation, please contact the author.
REFERENCES


APPENDIX

Included below are the initial raw OIM images before rotation correction, colored in inverse pole figure maps. Layers 1-5 are not included because they included errors due to variations in the SEM setup.

Figure A.1: Layer 6
Figure A.2: Layer 7
Figure A.3: Layer 8

Figure A.4: Layer 9

Figure A.5: Layer 10

Figure A.6: Layer 11
Figure A.7: Layer 12

Figure A.8: Layer 13

Figure A.9: Layer 14

Figure A.10: Layer 15
Figure A.11: Layer 16

Figure A.12: Layer 17

Figure A.13: Layer 18

Figure A.14: Layer 19
Figure A.19: Layer 24

Figure A.20: Layer 25

Figure A.21: Layer 26

Figure A.22: Layer 27
Figure A.23: Layer 28

Figure A.24: Layer 29

Figure A.25: Layer 30

Figure A.26: Layer 31
Figure A.27: Layer 32

Figure A.28: Layer 33

Figure A.29: Layer 34

Figure A.30: Layer 35
Figure A.31: Layer 36

Figure A.32: Layer 37

Figure A.33: Layer 38

Figure A.34: Layer 39
Figure A.39: Layer 44

Figure A.40: Layer 45

Figure A.41: Layer 46
Included below are the OIM maps from the square samples heat treated at different levels.

Figure A.42: Side 1, 4hr heat treat.

Figure A.43: Side 2, 4hr heat treat.
Figure A.44: Side 3, 4hr heat treat.

Figure A.45: Side 1 8hr heat treat.
Figure A.46: Side 2 8hr heat treat.

Figure A.47: Side 3 8hr heat treat.
Figure A.48: Side 1, 20 hr heat treat.

Figure A.49: Side 2, 20 hr heat treat. Data from side 3 of the 20 hr. heat treat is missing. It is speculated that the differences in grain size in the different heat treats are due to the heat treat but also due to possible variance in the sample.