THE INFLUENCE OF GRAIN BOUNDARY NETWORK STRUCTURE ON INTERGRANULAR CREEP CAVITATION OF OFHC COPPER

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Abstract

The prospect of structural failure, in proposed OFHC copper nuclear waste canisters, initiated by intergranular creep cavitation has prompted an investigation into the possibility of cavitation resistance enhancement through grain boundary engineering (GBE). In order to successfully implement GBE, the influence of the grain boundary network structure on creep cavitation must be ascertained. For this purpose, post-creep test characterization, using the electron backscatter diffraction technique, was performed on cavitated and non-cavitated grain boundary and triple junction structures. The implication of the findings were discussed in reference to the Coincident Site Lattice framework for grain boundaries and Bollmann’s I-line / U-line model for triple junctions.

Grain boundary characterization revealed that creep cavitation occurred primarily along a path of random boundaries. It was also determined that low angle (Σ 1) and twin (Σ 3) boundaries were the more cavitation resistant than random and other higher Σ CSL (Σ 5-29b) boundaries. The lack of observed cavitation selectivity between random and Σ 5-29b boundaries was attributed to the fact that creep conditions might be too severe. This may also explain the lack of selectivity of U-lines as preferential sites for cavity nucleation observed in this thesis. The findings of this thesis, however, do illustrate that there is grain boundary structural influence on intergranular creep cavitation of OFHC copper.
To My Girlfriend, Caren, who was with me
Every step of the way.
Thanks.
Always!
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1. Introduction

1.1 Creep of Nuclear Waste Canister Research

Oxygen Free High Conductivity (OFHC) copper has been selected as one of the prime candidate materials for the production of nuclear waste canisters. These canisters are to be used for long term storage of spent nuclear fuel rods in a deep underground vault. The conditions which these canisters will be placed under are as follows\(^1\). It is projected that the ambient temperature of the nuclear waste canister will be approximately 100°C. It is also expected that as a result of returning previously evacuated groundwater, there will be about 12 MPa of hydrostatic pressure exerted on the canisters. In the past, research into the durability of nuclear waste canister, has primarily focused on the corrosion resistance of the different candidate materials to groundwater\(^1\). However, the required long lifetime (~1000 years), combined with the aforementioned vault conditions raise the concern that Coble creep (due to low temperatures and low strain rates) will occur. Given sufficient time, Coble creep could cause the premature structural failure of these canisters; initiated by intergranular creep cavitation.

1.2 Intergranular Creep Cavitation

Intergranular creep cavitation begins with void nucleation; which occurs at locations of high stress concentrations along the grain boundary network\(^2\) (such as grain boundary ledges and particles, and triple junctions). Such locations of high stress concentrations
are illustrated schematically in Figure 1. The process of void nucleation can occur as an indirect consequence of Coble creep\textsuperscript{3}. This is since Coble creep can result in the occurrence of grain boundary sliding (GBS)\textsuperscript{4,5}, which may be the mechanism responsible for the nucleation of voids (as shown in Figure 1). The next step in intergranular cavitation is the growth of these stable voids into cavities, which can also proceed by grain boundary sliding. However, it has been suggested that void growth could also be a result of the absorption of nearby vacancies: which diffuse through the grain boundary as a result of stress-motivation\textsuperscript{6}. The continued growth of cavities, will eventually lead to the formation of microcracks due to cavity impingement. Here, the deformation mechanisms responsible for this process of cavity coalescence are still grain boundary sliding and diffusion.

![Figure 1 Schematic diagram showing various possible void nucleation mechanisms by GBS at locations of high stress concentrations: (a) at a triple junction (resulting in a wedge shape cavity); (b) at a grain boundary (from left to right): grain boundary ledges, due to particle fracture and particle decohesion (Adopted from ref. (7))](image-url)
1.3 Improving Cavitation Resistance by Grain Boundary Design and Control

From the previous section on intergranular creep cavitation, it can be realized that the key to improving the intergranular creep cavitation resistance lies in improving the resistance of OFHC copper to grain boundary sliding and also grain boundary diffusion. This may be achieved through grain boundary design and control.

Grain boundary design and control was first suggested by Watanabe\textsuperscript{8} in 1984. It is based on the fact that grain boundaries with different structures behave differently, as indicated in a review by Aust\textsuperscript{9}. Some boundaries will exhibit deleterious properties and some will exhibit "special properties". It has been indicated, in the same review, that boundaries which fall into the low \( \Sigma (\Sigma \leq 29b) \) CSL category when described by the CSL framework\textsuperscript{10} exhibit special properties. \( \Sigma \) is the numerical index describing the lattice matching at grain boundaries. Conversely, CSL boundaries described by \( \Sigma \) values greater than 29\textsuperscript{11} have, in general, been observed to display no "special" properties and have been classified as "random" boundaries. The idea is then to enhance the frequency of low \( \Sigma \) CSL ("special" boundaries) in a given material in order to improve the bulk properties of the material.

Grain boundary design and control can (and should) also be extended to triple junctions which are also part of the grain boundary network. This is due to two reasons. The first reason is analogous to "special" and random grain boundary behaviour. Triple lines with, what has been called I-line structure, have been observed to display improved properties
over triple lines with more of a defect-like character (or the U-lines)\textsuperscript{12,13}. The second reason is that the structure of the triple line is the result of the interaction among the grain boundary dislocations of each individual intersecting grain boundary. The significance of this is realized by the fact that the clustering of special grain boundaries has been observed to result in more triple lines with I-line structures\textsuperscript{14,15}.

1.3.1 Special Boundaries and Special Triple Junctions in Relation to Intergranular Cavitation

It is expected that "special" grain boundaries and "special" triple junctions (I-lines), due to comparatively more perfect structure, should be more resistant to intergranular cavitation than random grain boundaries and U-line triple junctions, respectively. Evidence supporting such a claim has been presented in other research dealing with the influence of grain boundary network structure on GBS\textsuperscript{16,17}, grain boundary diffusion\textsuperscript{18,19}, and the mechanical strength of triple junctions\textsuperscript{13}. These experiments show that grain boundary sliding and vacancy diffusion are more difficult in low $\Sigma$ CSL boundaries and that I-lines are stronger than U-lines. Other experimental evidence showing explicitly that special boundaries are more resistant to cavitation than random boundaries, has been presented by Lim and Raj\textsuperscript{20} for nickel, and Don and Majumdar\textsuperscript{21} for type 304 stainless steel.
1.3.2 Successful Application of Grain Boundary Design and Control

One should realize that grain boundary design and control is not necessarily applicable for all situations requiring some sort of material property enhancement. Successful application of grain boundary design and control requires that:

1. The phenomenon is intergranular in nature.
2. There is a grain boundary structural influence on the phenomenon.
3. The amount of enhancement required to produce an improvement in the material bulk properties is known and attainable.

This thesis will focus on the first two criteria in an effort to pave the way for the third criterion to be examined by future creep tests on grain boundary designed and controlled OFHC copper material. The first criterion (is it a grain boundary phenomenon?) can be readily examined through basic metallography. However, establishing whether there exists a grain boundary structural influence on the phenomenon (intergranular creep cavitation) requires a more extensive experimental and theoretical approach.
2. THEORETICAL BACKGROUND

2.1 Grain Boundaries

2.1.1 Grain Boundary Structure

The grain boundary can be defined as the region of contact between two differently oriented similar adjacent crystal lattices. Since the lattices of both crystals are similarly ordered and can be thought of as rigid, the structure of the boundary is dictated by the relative orientation of the two adjoining crystals. In general, in a polycrystalline material, as a result of the multitude of different adjacent grain orientations, there exists a wide spectrum of grain boundary structures. Previous research has already shown that within a given polycrystalline material, as a result of these structural differences, grain boundary behaviour could differ from boundary to boundary. Conversely, it is expected that boundaries with a similar structure or 'character' should behave in the same fashion.

2.1.2 Study of the Relationship Between Grain Boundary Structure and Behaviour

At this point, it should be noted that investigating the behaviour of a single grain boundary by determining the actual atomic arrangement at that boundary (by High Resolution Electron Microscopy, Transmission Electron Microscopy (TEM), or any other experimental method) is quite tedious and time consuming. Thus, past research relating the two, has generally be conducted via comparison of experimental results with theoretical understanding and modeling of grain boundary structure. Due to the time frame and the limited number of samples provided for this thesis, this path was chosen.
2.1.3 Grain Boundary Characterization

Normally, the macroscopic description of grain boundary geometry is derived through mathematical means using crystal orientations determined from crystallographic diffraction patterns. In order to fully describe or characterize a grain boundary, two variables are necessary; the misorientation between the two adjacent lattices and the orientation of the grain boundary plane. This is done using five independent parameters; three of which are used to describe the relative misorientation between the two adjoining grains and the remaining two are used to specify the orientation of the boundary plane normal with respect to either one of the two grains.

The relative misorientation or 'grain boundary misorientation' as it is known, is the 'angle' of rotation that transforms the unit orthonormal crystallographic axes of one crystal (grain 1) to or parallel to that of the adjacent second crystal (grain 2). Geometrically, the misorientation can be determined using a three by three rotation matrix, \( R \), with elements which are column vectors of directional cosines between the crystallographic axes of the two adjacent lattices. From \( R \), an angle-axis pair can be determined, which is commonly used to characterize grain boundaries. The 'angle' of rotation is determined from the trace of the rotation matrix:

\[
\theta = \cos^{-1} \left( \frac{(a_{11} + a_{22} + a_{33} - 1)/2}{1} \right) \quad \{1\}
\]

and the direction of the axis of rotation, \( <u,v,w> \) is determined from:

\[
<(a_{32} - a_{23}), (a_{13} - a_{31}), (a_{21} - a_{12})> \quad \{2\}
\]
where $a_{ij}$ are elements of $\mathbf{R}$. It should also be noted that the rotation matrix $\mathbf{R}$, possesses volume conserving properties and as such, should have a determinant of positive one.

2.1.4 Disorientation

The characterization of grain boundary misorientation using angle-axis pairs could be further refined with the concept of disorientation, which uses a single angle-axis pair to represent a group of equivalent grain boundaries. This is useful for cubic lattice systems whose 24 possible symmetry operations on a single grain boundary could lead to 576 equivalent representations of the same boundary. Recall that boundaries with similar or equivalent structure behave in similar fashion. Thus, it would simplify research dealing with the relationship between grain boundary structure and properties, if a group of equivalent boundaries can be characterized or described by a single angle-axis pair. The properties of this angle-axis pair are that the angle is the lowest of the misorientation angles ($\theta_{\text{min}}$) and that the axis must be confined to the standard stereographic triangle (SST), ((001), (110), (111)). As a result of the latter constraint, there are finite limits to the disorientation angles. The range of $\theta_{\text{min}}$, within the SST, calculated by Mackenzie\textsuperscript{25} and Handscomb\textsuperscript{26}, are: $45^\circ$ for $<100>$, $60^\circ$ for $<111>$ and $60.72^\circ$ for $<110>$, with a maximum of $62.80^\circ$ for $<552>$. 
2.2 Coincident Site Lattice Model

A further way of characterizing grain boundaries is through the use of the coincident site lattice (CSL) model, first proposed by Kronberg and Wilson\textsuperscript{10} in 1949. They suggested grain boundaries could be geometrically modeled as two interpenetrating lattices (grains), one rotated relative to the other about a common lattice point. Because the lattices in question are similarly ordered and rigid, it is expected that at certain angles of rotation, there would exist certain lattice sites which are coincident to both lattices. The superlattice formed from these shared atomic sites forms the CSL lattice. Using this model, any grain boundary could be modeled if the unit cell of the superlattice was to theoretically approach infinite dimensions\textsuperscript{27}.

The degree of lattice matching resulting from the relative rotation of the two grains is represented numerically by what is known as the ‘coincidence index’ or $\Sigma$. For cubic structures, $\Sigma$ is an odd integer and is given by:

$$\Sigma = \frac{\text{density of ordinary lattice points}}{\text{density of CSL points}} \quad \{3\}$$

which is also the volume fraction of the coincident unit cell relative to the perfect lattice unit cell. Figure 2 shows examples of $\Sigma 5$ and $\Sigma 17$ CSL lattices.

A mathematical relationship between $\Sigma$ values and angle-axis pairs for cubic lattices was first developed by Ranganathan\textsuperscript{28}. Because $\Sigma$ values are determined only by the relative ‘misorientations’ of two adjoining crystals, a standard list of cubic system CSL boundaries and their respective disorientation angle-axis pairs could be produced.
Figure 2 Schematic diagrams showing a) Sigma 5 and b) Sigma 17 CSL lattices formed by rotating two interpenetrating simple cubic (001) planes about the [001] direction. The CSL lattice is outlined with bolder lines.
Mykura\textsuperscript{24} has compiled a list of CSL boundaries from \(\Sigma1\) to \(\Sigma101e\). Letters are employed in increasing order (a,b,c \ldots) and are placed after the coincidence index value to denote CSL boundaries of increasing disorientation angles but having the same \(\Sigma\) values.

2.2.1 Properties of Low \(\Sigma\) CSL Boundaries

Although all grain boundaries can theoretically be classified using the CSL model, it has been suggested that boundaries with a coincidence index of \(\Sigma \leq 29\) (low \(\Sigma\) CSL boundaries) possess properties which are generally more desirable than those with \(\Sigma > 29\)\textsuperscript{11}. These “special” properties observed in low \(\Sigma\) grain boundaries (presented in a review by Palumbo and Aust\textsuperscript{29}) include:

1. Greater grain boundary sliding, fracture and cavitation resistance;
2. Less susceptibility to solute segregation;
3. Lower energy in pure metals;
4. Greater mobility, with specific solutes in a certain concentration;
5. Smaller diffusivity;
6. Lower intrinsic electrical resistivity; and
7. Greater resistance to corrosion.

Thus, it is expected that these special boundaries should be more resistant to intergranular cavitation.

2.2.2 Deviation From Exact CSL Relationship

In the review previously mentioned (by Palumbo and Aust\textsuperscript{29}) it was indicated that boundaries which slightly deviate from the exact CSL misorientation relationship have been found to somewhat preserve the periodic nature of the grain boundary through the
introduction of an array of intrinsic grain boundary dislocations (IGBD) into the grain boundary structure. Such discrete intrinsic grain boundary dislocations have been observed by TEM\textsuperscript{30,31}. Thus, the structure of the deviated boundary can be described as one containing segments of low $\Sigma$ CSL boundary structure separated by IGBD cores. Because the periodic structure of the CSL boundary is somewhat preserved, the special properties of the corresponding ideal CSL boundary from which the structure deviates, is retained\textsuperscript{32}.

However, it should be noted that there exists a certain point where the periodicity of the boundary cannot be maintained by the introduction of more IGBD’s. This is the point where the dislocation spacing is so small that dislocation core overlap occurs, completely eliminating the periodic nature of the boundary. At this point the grain boundary can be considered to possess general or random structure and it follows that the boundary behaves similarly to a random boundary. Mathematically, such a limit is determined in general by formulae derived from the Read-Shockley equation for low angle boundaries (as given, for example, in ref. 33):

$$2 \sin \left( \frac{\theta}{2} \right) = \frac{b}{d} \quad \{4\}$$

where $\theta$ is the misorientation angle between the two lattices, $b$ is the Burgers vector of the grain boundary dislocations (GBD) and $d$ is the spacing of these dislocations.

There exist several different criteria, which give the maximum allowable deviation ($\Delta\theta$) as a function of the $\Sigma$ value of grain boundary. The most commonly applied, Brandon’s criterion\textsuperscript{34}, is given by:
\[ \Delta \theta = \theta_0 \Sigma^{-1/2} \quad \{5\} \]

where \( \theta_0 \), the maximum angle of deviation is 15° and \( \Delta \theta \) is the maximum allowable angle of deviation. A more restrictive criterion for misorientation deviation from exact CSL relationships is the Palumbo-Aust\textsuperscript{35} criterion:

\[ \Delta \theta = \theta_0 \Sigma^{-5/6} \quad \{6\} \]

where \( \theta_0 \) is 15°.

The significance of the two criteria mentioned is that grain boundaries while considered to be low \( \Sigma \) CSL boundaries under Brandon’s criterion could be considered random when the Palumbo-Aust criterion is applied. This is since boundaries falling outside the Palumbo-Aust criterion may be still within Brandon’s criterion. Evidence suggesting that such boundaries may indeed be random grain boundaries, and therefore, no longer possessing “special properties”, has been provided through geometrical considerations and corrosion findings\textsuperscript{35}. Moreover, in recent work performed by Pan et. al.\textsuperscript{36} in Alloy X-750, it was observed that such boundaries were vulnerable to intergranular stress corrosion cracking. These findings suggest that perhaps the more appropriate criterion to use is the Palumbo-Aust criterion. However, since Brandon’s criterion is still widely used in the literature, it will also be used in this thesis, in addition to the Palumbo-Aust criterion.
2.3 Triple Junctions

2.3.1 Triple Junction Structure

The triple line, as mentioned in the introduction section, is the intersection of three grain boundaries. If the structure of each individual grain boundary can be described as arrays of grain boundary dislocations (GBD), as is done with the O-lattice model\textsuperscript{37}, then the structure of the triple line is dictated by the interaction of the GBD's of all three grain boundaries. It has been illustrated through modeling using the O-lattice model, that the interaction of GBD's at the triple line results in two structural configurations. The first is where the interaction of grain boundary dislocations results in a nodal balance at the triple line. The other is where the interaction does not result in a nodal balance at the triple line. It has been illustrated that the latter structural configuration can be considered more of a defect\textsuperscript{38} and may thus be a preferential site for cavity nucleation\textsuperscript{13}.

2.3.2 Characterization of Triple Lines

The characterization of triple lines (in essence, the determination of whether there is nodal balance of GBD's at the triple line) is done by performing a sequence of
misorientation type transformations around the triple line in a counter-clockwise fashion\(^\text{39}\) (see Figure 3). The sequence of transformations is performed relative to a reference point, and starts and ends with the same grain. The choice of starting grain is irrelevant as the character of the triple line cannot change (since it is determined by the interaction of the three GBD arrays which in turn do not change). The resultant matrix, if it is the identity matrix, then means that there exists a GBD nodal balance at the triple line and the triple line can be classified as an I-line. On the other hand, if the resultant matrix is not an identity matrix, then the triple line is considered a U-line.

However, if one were to follow the above procedure, the sequence of transformations, \(R_aR_bR_a\), which is actually \(R_1R_3^{-1}R_3R_2^{-1}R_2R_1^{-1}\), would always lead to an identity matrix. But, there is one more factor to be taken into consideration that would alter the validity of
this last statement. That is the assumption that the GBD's of the individual GBD networks would always arrange themselves into the lowest energy configuration. This is mathematically calculated by determining what Bollmann calls the nearest neighbour relationship and applying it to each grain boundary structure.

2.3.2.1 Nearest Neighbour Relationship (NNR)

The nearest neighbour relationship is defined by Bollmann as the transformation of one lattice to that of the adjoining lattice such that it results in the largest inter-spacing of grain boundary dislocations. This transformation is mathematically arrived at through the use of a unimodular matrix \( U \) to operate on a general transformation (for example a rotation matrix, \( R \)). This corresponds to multiplying the transformation expressed in crystal coordinate system by the unimodular matrix on the right hand side \( RU \). This has the effect of interchanging column vectors such that the trace \( (1 + 2 \cos(\theta)) \) is maximized; which corresponds to the smallest angle of rotation \( \theta \). The algebraic procedure is as follows:

1. Transformation of \( R_a \) to reference coordinates (grain 1 is chosen as a reference to make calculations easier)

\[
R_a' = R_1^{-1}R_aR_1 = R_1^{-1}R_2 \\
\text{(7)}
\]

2. Transformation of \( R_a' \) into crystal coordinate system via the structure matrix \( S \)

\[
R^* = S^{-1} R_1^{-1} R_2 S \\
\text{(8)}
\]

The structure matrix for an fcc material, as listed by Palumbo, is:
where \( a \) represents the lattice constant of the material.

3. From \( \mathbf{R}^* \), the external (\( \mathbf{M}_e \)) and internal matrix (\( \mathbf{M}_i \)) are extracted such that

\[
\mathbf{M}_e + \mathbf{M}_i = \mathbf{R}^* \quad \{10\}
\]

The elements of \( \mathbf{M}_i \) are positive between 0 and 1; while the elements of the external matrix are integers which could be positive or negative.

4. The next step involves calculating the geometric tensor.

\[
\mathbf{G} = \mathbf{S}^T \mathbf{S} \quad \{11\}
\]

5. From the unit cell, three of the eight corner coordinates ((000), (001), (010), (010), (101), (011), (111)) are tentatively selected (one corner coordinate for each of the three column vectors in the internal matrix (\( \mathbf{M}_i \)). The unit cell corners selected are the coordinates in closest proximity to the column vectors. The smallest square of this distance (\( d_i^2 \)) can be determined through iterative calculations using the equation:

\[
d_i^2 = [\mathbf{G}^* (\mathbf{x}_i - \mathbf{x}_c)] * (\mathbf{x}_i - \mathbf{x}_c) \quad \{12\}
\]

where \( \mathbf{G} \) is the metric tensor calculated in step 4, \( \mathbf{x}_i \) \((i = 1, 2, 3)\) corresponds to the first, second and third column vectors of \( \mathbf{M}_i \) respectively and \( \mathbf{x}_c \) represents the eight unit cell corners.

6. The selected three unit cell coordinates are then put in a 3X3 matrix as column vectors in the order of \([d_1^2, d_2^2, d_3^2]\) and added to the external matrix to form a new matrix \( \mathbf{M} \).

7. \( \mathbf{M} \) is the inverse of the unimodular matrix and as a result should have a determinant of positive one. Should the determinant not be positive one, step 5 must be redone.
selecting a different unit cell corner coordinate of slightly further proximity to the
column vector(s) of the internal matrix which would make the determinant of \( M \)
positive one.

8. The unimodular matrix is then the inverse of \( M \) or

\[
U_a = M^{-1}
\]  \{13\}

9. And the nearest neighbour transformation of \( R_a' \) is

\[
R_a'' = R_a' U_a
\]  \{14\}

This procedure may be applied to \( R_b \) and \( R_c \) if necessary.

2.3.2.2 Incorporating the NNR into Triple Line Calculations

Continuing with the characterization of the triple line, the resulting NNR for grain
boundaries a, b and c are then converted back to grains 1, 2 and 3 respectively
(e.g. \( R_a''' = R_1 R_2' U_a R_1^{-1} \)). The sequence of operations previously mentioned is carried
out which then becomes

\[
R_1 U_c R_3^{-1} R_3 U_b R_2^{-1} R_2 U_a R_1^{-1}
\]  \{15\}

This entire expression is then transformed back to the reference orientation

\[
R_1^{-1} R_1 U_c R_3^{-1} R_3 U_b R_2^{-1} R_2 U_a R_1^{-1} R_1
\]  \{16\}

and equation 15 then reduces to

\[
T = U_c U_b U_a
\]  \{17\}

Should \( T \) (equation 17) result in an "identity" matrix, meaning that nodal balance is
achieved through the interaction of the GBD arrays, the triple junction can be classified as
an I-line. Otherwise, the triple junction is considered a U-line. It should be noted that in
certain situations, there may be multiple solutions or different T’s. In such a situation, the characterized triple junction is considered a U-line only if all the possible T’s are not the identity matrix. On the other hand, if any of the possible T’s are the identity matrix, then it quite possible that the triple junction in question is an I-line. In this case, the triple junction is assumed to possess I-line structure.
3. OBJECTIVES

The objective or focus of this thesis is to establish if there is a grain boundary network (grain boundary and triple junction) structural influence on intergranular creep cavitation of OFHC copper. This is to be accomplished by the characterization of cavitated and non-cavitated grain boundary and triple junction structures, using the CSL and I-line / U-line models to determine if low $\Sigma$ CSL boundaries and I-line triple junctions in polycrystalline OFHC copper are resistant to intergranular cavitation. For this purpose, samples which had been crept at slightly elevated temperatures will be examined.
4. EXPERIMENTAL PROCEDURE

4.1 Creep Testing

The service conditions which the nuclear waste canisters are expected to encounter have previously been mentioned in the introduction section (section 1.1). Ideally, in order to observe, in a laboratory setting, any effects that the service conditions might have on the canisters, one has to try to simulate as closely as possible the same conditions. Unfortunately, there have been no creep tests performed to date under these conditions (~12 MPa stress and temperatures ranging from 100°C to 200°C). However, samples which had been creep tested at higher stresses, while still in the temperature range in question, were made available by Ontario Hydro Technologies (OHT). Three of these creep samples were provided for this thesis. The creep conditions for these samples are listed in Table 1 and the creep curves for samples 1, 2 and 3 are shown in appendix 1.

An Ashby deformation map for pure copper with a typical grain size of 100 μm is shown in Figure 4. Based on the information provided in Table 1, the locations on the map at which the creep tests were conducted, were determined (see appendix 2 for equations and calculations used). These "locations" are marked on the map with X's.
Table 1 Creep test conditions and total strain of specimens provided

<table>
<thead>
<tr>
<th>Creep Test Number</th>
<th>Temperature (°C)</th>
<th>Stress (MPa)</th>
<th>Total Strain</th>
<th>Total Time (h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>100</td>
<td>52.0</td>
<td>2.589E-3</td>
<td>17356</td>
</tr>
<tr>
<td>2</td>
<td>100</td>
<td>64.5</td>
<td>1.97E-2</td>
<td>10400</td>
</tr>
<tr>
<td>3</td>
<td>150</td>
<td>64.5</td>
<td>1.57E-3</td>
<td>211</td>
</tr>
</tbody>
</table>

Figure 4 Ashby Map for pure copper with an average grain size of 100 micrometers. The X’s mark the locations on the map where the three creep tests were conducted. Adopted from Ref. 42.
From Figure 4, it can be noted that the samples were tested in the lower end of the power-law regime. However, it is possible that grain boundary effects may still play a role in this regime. Thus, the three provided samples were deemed suitable for study in this thesis.

### 4.2 Chemical Composition

Table 2 is a list of the main impurities and their concentrations determined from a chemical composition analysis performed by OHT. According to the ASTM standard B170\(^4\), the concentration of impurities found in certified Grade 2 oxygen free copper (C10200), must be less than 0.05% combined. This value includes a permissible oxygen concentration of 10 ppm, but excludes silver. The balance of the composition (99.95%) is then made up of copper and silver. The total concentration of impurities listed in table 2 is 0.024% which is below the permissible limit of 0.05%. Although there are other impurities which have not been analyzed for by OHT, the concentration of oxygen has been ascertained to be 0.00096%. This is slightly lower than the permissible limit set out by the ASTM B170 Standard. From this, it may be said that the copper material used by OHT for their creep tests was grade 2 oxygen free copper (C10200). Nevertheless, for the purpose of consistency, the copper rods will still be referred to as OFHC copper.
Table 2 Table listing the impurities and their levels detected in the copper samples used in this study

<table>
<thead>
<tr>
<th>Impurity</th>
<th>Concentration (OHT)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P</td>
<td>&lt;0.010%</td>
</tr>
<tr>
<td>Ag</td>
<td>0.0060%</td>
</tr>
<tr>
<td>Bi</td>
<td>&lt;0.0050%</td>
</tr>
<tr>
<td>Fe</td>
<td>0.0007%</td>
</tr>
<tr>
<td>Pb</td>
<td>&lt;0.0010%</td>
</tr>
<tr>
<td>O₂</td>
<td>0.00096%</td>
</tr>
<tr>
<td>S</td>
<td>0.0007%</td>
</tr>
</tbody>
</table>

4.3 Material Processing History

The samples provided by OHT were machined from extruded copper rods. However, no further material processing history was provided regarding the origin of the rods. The typical processing for the production of copper rods involves extrusion from a hot billet and coiling. Following this, the coiled copper is cold drawn to size and temper in straight lengths.

4.4 Sectioning of Creep Test Samples

Sectioning and mounting of the samples provided by OHT was performed as shown schematically in Figure 5. Note that samples were labeled in the following fashion: Sample number - Section number. Sample numbers A, 1, 2 and 3 represent as-received, creep test 1, test 2, test 3 samples, respectively.
4.5 Metallographic Preparation

Two techniques were employed in the metallographic preparation of the creep specimens in order to observe two different features: 1) cavities at grain boundaries; and 2) cavities associated with triple junctions.

Technique 1: This was a standard grinding and polishing technique. Samples were ground to 2400 grit SiC and then polished with 1 micron diamond paste. The samples were then electropolished in Struer's D2 electropolishing solution (see appendix 3 for composition and electropolishing parameters) to remove the surface deformation layer in order to produce better diffraction patterns.

Technique 2: A different polishing technique (without electropolishing) was required in order to examine cavities at triple junctions. This was done since electropolishing was found to preferentially dissolve triple junctions which made the detection of creep cavities at triple junctions very difficult.
Figure 5 Schematic diagram illustrating how the samples were sectioned and mounted

The procedure essentially involved reducing the number of grinding and polishing steps, pressure and time (with the exception of fine vibratory polishing) to minimize the amount of deformation from grinding and polishing. The steps were:

1. Grind using 600 grit SiC paper for 40 seconds, 800 grit SiC paper for 40 seconds;
2. 6 micron diamond paste polishing for about 4 minutes; and
3. Vibratory polishing using 0.05 micron polishing solution (MasterPrep2™) diluted with water (50%) for approximately 6 hours. This was done to slowly remove the deformed layer from the 6 micron diamond paste polish. No weights were added to the weight of the sample holder itself.

4.6 Cavitation Investigation

The bulk of the experimental work involved in this thesis was the determination of grain orientations through the use of Electron BackScatter Diffraction (EBSD) Patterns (done in a SEM environment). Results obtained from the grain orientation work could then be used to characterize both grain boundaries and triple junctions which is the main objective of this thesis. Optical examination of polished axial cross sections, 1 - 4, (both techniques) showed a minute amount of cavitation. Thus, only the transverse sectioned samples, 5 and 6, which showed considerable cavitation were used for cavitation analysis.

4.7 Electron BackScatter Diffraction (EBSD) Patterns or Kikuchi Patterns

Although the technology used to generate and index EBSD patterns has progressed to the point of full automation, the science behind the generation of EBSD patterns still remains the same. Figure 6 is a schematic diagram of the apparatus involved in collecting and ‘indexing’ of EBSD patterns. EBSD patterns are generated by directing a beam of electrons to a highly tilted specimen (70.5° about an axis normal to the imaginary plane
formed using the axes of the electron beam and that of the low light camera). Some electrons penetrate the surface and impinge on a crystallographic plane which would subsequently diffract. The diffracted electrons fall onto the phosphor screen producing a pair of Kikuchi lines (Kikuchi band). It should be realized that there are other planes in the crystal, as well, which will also simultaneously diffract electrons onto the surface of the phosphor screen. The combination of all these diffraction lines (Kikuchi bands) results in an EBSD pattern.

Figure 6 Schematic diagram of an EBSD system with all its components.

However, the electrons diffracted represent only a small fraction of the total number of electrons actually hitting the phosphor screen. These non-diffracting electrons, combined with stray electrons, in the microscope actually result in background noise, which diminishes the quality of the diffraction pattern. Obviously, this makes it more difficult
to analyze and index the pattern. Thus, an image enhancer is employed to remove the background noise and increase the signal-to-noise ratio of the diffraction patterns. The enhanced image is then captured by the computer which uses computer algorithms to detect the exact location of the Kikuchi lines.

4.7.1 The Semi-Automated Approach

For the semi-automated approach, the computer superimposes graphically what it deems to be the correct solution over the captured diffraction pattern. This simulated diffraction pattern represents an orientation relative to the common reference point for all diffraction patterns. The operator would then verify the solution (does the simulated Kikuchi pattern match the actual pattern?). Assuming the solution is correct, the orientation of the grain as determined from the diffraction pattern is then recorded by the computer. The operator would then move the ‘location’ of the beam to another spot which yields a distinctively different diffraction pattern. And the process is repeated to measure crystallographic orientations in as many locations as desired.

4.7.2 Orientation Imaging Microscopy

The fully automated approach to collecting and indexing EBSD patterns (grain orientations) has been named Orientation Imaging Microscopy, or OIM for short. The procedure is almost identical to the semi-automated approach. The important differences are:
1. The computer moves the location of the beam, according to grid parameters preset by the operator.

2. The operator does not verify that the solution given by the computer for any particular diffraction pattern is correct. Instead, a confidence index and a value for image quality are assigned to identify the deviation from correct solutions.

3. A map of the microstructure (computer generated) can be produced which would otherwise have required etching to produce (micrograph).

4. Each of the pixels on the map represents an indexed orientation which can be called upon later by computer software to be used, for example, in the characterization of grain boundary and triple junction structures. The crystallographic orientation data can also be used to generate texture maps or pole figures.

4.8 Data Classification

For the purpose of data analysis in this thesis, the results obtained from EBSD patterns are classified into three parts: i) OIM runs to determine overall Grain Boundary Character Distribution (GBCD) and overall I-line frequency, ii) intergranular cavities and iii) triple junctions associated with cavitation.

4.8.1 OIM Runs

OIM runs were performed on specimens A-6, A-2, 1-2, 1-6, 2-2, 2-6, 3-3, 3-6 (see Figure 5). The OIM 1.5 version of software produced by TexSEM Laboratories (TSL) was used
to conduct these runs and also to provide statistics with regards to the overall GBCD.

The software was also used to procure two other pieces of information. The first being the average grain size (which was verified later from micrographs using the linear intercept method). The other was the overall distribution of I-lines (triple junctions) from microstructural maps produced using the software.

4.8.2 Intergranular Cavities and Triple Junction Cavities

For the purpose of investigating cavitated boundaries and triple junctions, the aforementioned semi-automated approach was used. In order to better reveal intergranular cavities, metallographic technique 1 (with electropolishing) was employed. However, only relatively large intergranular cavities could be examined since the electropolishing made it impossible to distinguish between creep cavities and electropolishing pits at triple junctions. 50 such cavities were analyzed using a semi-automated EBSD system on a conventional Jeol JSM 840 SEM. Boundaries along which the cavities occurred, as well as the non-cavitated boundaries connected to the cavitated ones were characterized. Using the same semi-automated approach but metallographic specimen preparation technique 2, and a Field Emission Microscope (FEM), an additional 32 cavities were examined.

In addition, 14 wedge shape (triangular) triple junction cavities were characterized.

Combining these 14 triple junctions with another 84 triple junctions selected from the 32 intergranular cavities examined in the FEM and the 50 intergranular cavities examined in
the conventional SEM, an average frequency of I-lines was obtained for 98 triple
junctions associated with cavities. All triple junctions were characterized using software
which was written initially by G. Palumbo\textsuperscript{41} and later modified by P. Fortier\textsuperscript{45}. 
5. RESULTS

5.1 Metallographic Observations

Metallographic observation revealed that the damage caused by creep was indeed intergranular in nature. This is visible in Figures 7 and 8. It was also observed that the cavities were uniformly distributed throughout the transverse sections of all samples. This illustrates that cavitation did not occur preferentially in localized areas of the sample.

![Figure 7](image-url)  
**Figure 7** SEM micrograph illustrating the intergranular nature of the creep cavities observed.
5.2 Intergranular Cavitation as a Function of Grain Boundary Type

5.2.1 Analysis Using Brandon’s Criterion

The frequencies of different cavitated boundary types as determined by the ‘semi-automated approach’ and using Brandon’s criterion (equation 5) are listed in Table 3. The results indicate that grain boundary cavitation, in the copper, as a result of creep deformation at slightly elevated temperatures occurs primarily on boundaries considered to be random in structure. This can be observed in Figure 9; which shows that the...
Figure 9 Distribution of different cavitated grain boundary types for all three creep samples
frequencies of cavitated random boundaries for all three crept samples is greater than that of the cavitated low $\Sigma$ CSL boundaries.

<table>
<thead>
<tr>
<th></th>
<th>Total</th>
<th>Random No.</th>
<th>Random (%)</th>
<th>$\Sigma$ 1 No.</th>
<th>$\Sigma$ 1 (%)</th>
<th>$\Sigma$ 3 No.</th>
<th>$\Sigma$ 3 (%)</th>
<th>$\Sigma$ 5 - 29b No.</th>
<th>$\Sigma$ 5 - 29b (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample 1-6</td>
<td>22</td>
<td>15</td>
<td>68.2</td>
<td>0</td>
<td>0.0</td>
<td>1</td>
<td>4.6</td>
<td>6</td>
<td>27.2</td>
</tr>
<tr>
<td>Sample 2-6</td>
<td>97</td>
<td>82</td>
<td>84.6</td>
<td>4</td>
<td>4.1</td>
<td>1</td>
<td>1.0</td>
<td>10</td>
<td>10.3</td>
</tr>
<tr>
<td>Sample 3-6</td>
<td>124</td>
<td>110</td>
<td>88.7</td>
<td>3</td>
<td>2.4</td>
<td>2</td>
<td>1.6</td>
<td>9</td>
<td>7.2</td>
</tr>
</tbody>
</table>

A more detailed examination of Figure 9 shows that as a group, there are more cavitated $\Sigma$ 5-29 b CSL boundaries than the number of cavitated $\Sigma$ 1 and $\Sigma$ 3 boundaries combined. It can also be observed in Figure 9 that the frequency of cavitated $\Sigma$ 5 - 29 b CSL grain boundaries is less than the frequency of cavitated boundaries determined to be random. Thus, from Figure 9 alone, it seems that random boundaries are less cavitation resistant than $\Sigma$ 5 - 29 b CSL grain boundaries; which in turn are less cavitation resistant than low angle ($\Sigma$ 1) and twin ($\Sigma$ 3) grain boundaries. However, there is a possibility, that the aforementioned observations are just the result of the overall GBCD. In other words, it is possible that the material tested contained more random boundaries than $\Sigma$ 5 - 29b CSL boundaries and more $\Sigma$ 5 - 29 b CSL boundaries than twin ($\Sigma$ 3) and low angle ($\Sigma$ 1) grain boundaries.

To check if the observed cavitation selectivity is independent of the number of each type of boundary present and instead dependent on the structure of the grain boundaries, a comparison between the cavitated boundary frequencies (Table 3) and the overall grain
boundary character distribution (Table 4) was made. This comparison is illustrated for creep test sample 2 in Figure 10. From Figure 10, it is shown that the distribution of cavitated grain boundary frequencies is different from the overall GBCD. This finding was also observed for the remaining two creep samples. Thus, this comparison serves to illustrate that there exists a structural influence on intergranular creep cavitation.

Table 4  Overall GBCD as determined by OIM fully automated EBSD approach (using Brandon’s criterion)

<table>
<thead>
<tr>
<th>Samples</th>
<th>Σ 1 (%)</th>
<th>Σ 3 (%)</th>
<th>Σ 5 - 29b (%)</th>
<th>Random (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A-4</td>
<td>50.4</td>
<td>14.8</td>
<td>4.7</td>
<td>30.0</td>
</tr>
<tr>
<td>A-6</td>
<td>50.6</td>
<td>15.7</td>
<td>4.7</td>
<td>28.9</td>
</tr>
<tr>
<td>1-2</td>
<td>57.7</td>
<td>11.0</td>
<td>3.6</td>
<td>27.6</td>
</tr>
<tr>
<td>1-6</td>
<td>68.0</td>
<td>10.6</td>
<td>2.0</td>
<td>19.2</td>
</tr>
<tr>
<td>2-2</td>
<td>57.2</td>
<td>14.6</td>
<td>3.2</td>
<td>24.9</td>
</tr>
<tr>
<td>2-6</td>
<td>62.5</td>
<td>13.8</td>
<td>2.5</td>
<td>21.4</td>
</tr>
<tr>
<td>3-3</td>
<td>61.0</td>
<td>12.6</td>
<td>2.6</td>
<td>23.7</td>
</tr>
<tr>
<td>3-6</td>
<td>65.8</td>
<td>9.0</td>
<td>3.0</td>
<td>23.3</td>
</tr>
<tr>
<td>Average</td>
<td>59.2</td>
<td>12.8</td>
<td>3.2</td>
<td>24.8</td>
</tr>
</tbody>
</table>

A more detailed examination of Figure 10 shows that overall frequencies are greater than the cavitated frequencies for low angle (Σ 1) and twin (Σ 3) grain boundaries. The reverse is observed for random and the group of Σ 5 - 29 b CSL grain boundaries. These observations suggest that low angle (Σ 1) and twin (Σ 3) boundaries are more creep cavitation resistant than random boundaries. However, the same cannot be said for the group of Σ 5 - 29 b CSL grain boundaries. This is since for both random and Σ 5 - 29 b CSL grain boundaries, their respective components in the cavitated grain boundary distribution are stronger than those found for the overall GBCD. This does, however,
Comparison of Cavitated Grain Boundary Types with GBCD as Determined by OIM of Sample 2 (Using Brandon's Criterion)

Figure 10 Comparison of cavitated grain boundary type frequencies with the overall GBCD for sample 2
suggest that low angle (Σ 1) and twin (Σ 3) grain boundaries are more resistant to cavitation than Σ 5 - 29 b CSL grain boundaries.

5.2.2 Analysis Using the Palumbo-Aust Criterion

Intergranular cavitation analysis using the Palumbo-Aust criterion (equation 6) was also performed and compared with the same analysis performed using Brandon's criterion (equation 5). The frequency distributions determined for the different cavitated grain boundary types are listed in Table 5. The overall GBCD's determined from the OIM runs, using the Palumbo-Aust criterion are provided in Table 6. From Table 5, it is immediately observed that for all three creep samples (1-6, 2-6, 3-6), almost all the cavitated grain boundaries characterized are now random grain boundaries. Conversely, very few cavitated grain boundaries were found to be low Σ CSL boundaries. A more detailed examination of Table 5 shows that for sample 1-6 and sample 3-6 none of the cavitated grain boundaries were determined to be twin (Σ 3) and Σ 5 - 29 b CSL boundaries. For sample 2-6, it is observed (Table 5) that only three cavitated boundaries were low Σ CSL grain boundaries (one twin (Σ 3) and two Σ 5 - 29b). The application of the Palumbo-Aust or Brandon's criterion does not change the number of cavitated grain boundaries determined to be low angle (Σ 1) grain boundaries. Thus, the frequencies of low angle (Σ 1) grain boundaries in Table 5 is identical as that for Table 3.
Table 5 Table listing the frequencies of different cavitated boundary types as determined using the Palumbo-Aust criterion

<table>
<thead>
<tr>
<th>Samples</th>
<th>Total No.</th>
<th>Random No. (%)</th>
<th>Σ 1 No. (%)</th>
<th>Σ 3 No. (%)</th>
<th>Σ 5 - 29b No. (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample 1-6</td>
<td>22</td>
<td>22</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Sample 2-6</td>
<td>97</td>
<td>90</td>
<td>4</td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>Sample 3-6</td>
<td>124</td>
<td>121</td>
<td>3</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

Table 6 Overall GBCD as determined by OIM fully automated EBSD approach (using the Palumbo-Aust criterion)

<table>
<thead>
<tr>
<th>Samples</th>
<th>Σ 1 (%)</th>
<th>Σ 3 (%)</th>
<th>Σ 5 - 29b (%)</th>
<th>Random (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A-4</td>
<td>50.4</td>
<td>9.5</td>
<td>0.5</td>
<td>39.6</td>
</tr>
<tr>
<td>A-6</td>
<td>50.6</td>
<td>10.4</td>
<td>0.6</td>
<td>38.4</td>
</tr>
<tr>
<td>1-2</td>
<td>57.7</td>
<td>6.7</td>
<td>0.4</td>
<td>35.2</td>
</tr>
<tr>
<td>1-6</td>
<td>68.0</td>
<td>5.8</td>
<td>0.2</td>
<td>26.0</td>
</tr>
<tr>
<td>2-2</td>
<td>57.2</td>
<td>8.6</td>
<td>0.3</td>
<td>33.8</td>
</tr>
<tr>
<td>2-6</td>
<td>62.5</td>
<td>8.3</td>
<td>0.3</td>
<td>28.9</td>
</tr>
<tr>
<td>3-3</td>
<td>61.0</td>
<td>7.3</td>
<td>0.2</td>
<td>31.5</td>
</tr>
<tr>
<td>3-6</td>
<td>65.8</td>
<td>5</td>
<td>0.2</td>
<td>28.8</td>
</tr>
<tr>
<td>Average</td>
<td>59.2</td>
<td>7.7</td>
<td>0.3</td>
<td>32.8</td>
</tr>
</tbody>
</table>

From Table 6, it is observed that the overall frequencies of random grain boundaries for samples 1-6, 2-6 and 3-6 are on average 28% which is not the case for the cavitated boundaries (Table 5). Again, the use of Brandon’s criterion or the Palumbo-Aust criterion does not alter the frequencies of the low angle boundaries, since the maximum deviation angle of 15° is equal for both criteria. Thus, it follows then that the overall GBCD is different from the frequency distribution of the cavitated boundaries of all three creep samples. A comparison of cavitated grain boundary type frequencies with the overall GBCD frequencies for twin boundaries, shows that the former is smaller than the latter. This is true for all creep samples. For the group of Σ 5 -29 b CSL grain
boundaries, and only for samples 1-6 and 3-6, the cavitated frequencies are lower than the overall frequencies (Table 6). However, the opposite is true for sample 2.

5.3 Crystallographic Texture

The crystallographic data obtained from the OIM runs were also used to determine the crystallographic texture of the specimens. For the axial cross-sections of the as-received specimen (A-4), as well as the crept specimens (1-2, 2-2, 3-3), the [111], [200] and [220] contour pole figures are shown in Figures 11 to 14. From these figures, it is seen that all cross-sectional samples show the [111], [200] duplex fibre texture usually observed in wires or extruded rods made from FCC materials. In addition, there is also a weak [220] texture component.

5.4 Triple Junctions

The overall distribution of triple junctions (expressed as % - I-lines) determined from the OIM runs is presented in Table 7 for all three samples. Table 8 lists the frequencies of I-lines for triple junctions associated with creep cavitation for the transverse sections of all three creep samples (1-6, 2-6, 3-6). Triple junctions with one, two and three cavitated grain boundaries were used for this analysis. An example of a triple junction with two cavitated grain boundaries is illustrated in Figure 8. From Table 8 it is observed that the frequency of I-lines associated with creep cavitation is slightly smaller than the overall
Figure 11  [111], [200] and [220] contour pole figures for the as-received extruded sample showing duplex fibre texture

Figure 12  [111], [200] and [220] contour pole figures for sample 1-2 showing duplex fibre texture
Figure 13 [111], [200] and [220] contour pole figures for sample 2-2 showing duplex fibre texture

Figure 14 [111], [200] and [220] contour pole figures for sample 3-3 showing duplex fibre texture
frequency of I-lines.

**Table 7** Frequency of triple junctions for all specimens as determined from OIM maps.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Total TJ Measured</th>
<th>I-lines Determined</th>
<th>Percentage I-line</th>
</tr>
</thead>
<tbody>
<tr>
<td>A-4</td>
<td>53</td>
<td>18</td>
<td>34.0</td>
</tr>
<tr>
<td>A-6</td>
<td>54</td>
<td>14</td>
<td>25.9</td>
</tr>
<tr>
<td>1-2</td>
<td>50</td>
<td>17</td>
<td>34.0</td>
</tr>
<tr>
<td>1-6</td>
<td>54</td>
<td>18</td>
<td>33.3</td>
</tr>
<tr>
<td>2-2</td>
<td>60</td>
<td>11</td>
<td>18.3</td>
</tr>
<tr>
<td>2-6</td>
<td>50</td>
<td>12</td>
<td>24.0</td>
</tr>
<tr>
<td>3-3</td>
<td>63</td>
<td>10</td>
<td>15.8</td>
</tr>
<tr>
<td>3-6</td>
<td>59</td>
<td>15</td>
<td>25.4</td>
</tr>
<tr>
<td>Total</td>
<td>(443)</td>
<td>(115)</td>
<td>26.0</td>
</tr>
</tbody>
</table>

**Table 8** I-line frequencies of all triple junctions examined, comparing those associated with cavitation with the overall I-line frequencies (taken from Table 7)

<table>
<thead>
<tr>
<th>Sample</th>
<th>Cavitated TJ (No.)</th>
<th>I-lines (No.)</th>
<th>I-lines (%)</th>
<th>Overall TJ (No.)</th>
<th>I-lines (No.)</th>
<th>I-lines (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample 1</td>
<td>10</td>
<td>2</td>
<td>20.0</td>
<td>54</td>
<td>18</td>
<td>33.3</td>
</tr>
<tr>
<td>Sample 2</td>
<td>44</td>
<td>8</td>
<td>18.1</td>
<td>50</td>
<td>12</td>
<td>24.0</td>
</tr>
<tr>
<td>Sample 3</td>
<td>44</td>
<td>7</td>
<td>15.9</td>
<td>59</td>
<td>15</td>
<td>25.4</td>
</tr>
<tr>
<td>Total</td>
<td>98</td>
<td>17</td>
<td>17.3</td>
<td>163</td>
<td>45</td>
<td>27.6</td>
</tr>
</tbody>
</table>

Previously, in the introduction section, it was suggested that triple junctions could act as high stress concentration sites for the nucleation of stable voids: which later grow and coalesce. An example of such a cavity is shown in Figure 15. Note that the lines in Figure 15 schematically show the three intersecting grain boundaries as determined from the changes in the electron diffraction pattern. Characterization of 14 such wedge shape cavities revealed that most (11) or 79% of the 14 wedge-shaped cavities were U-lines, suggesting therefore that U-line triple junctions might act as preferential void nucleation sites. However, it is seen that this frequency (79%) is quite similar to the average U-line
fraction found in the material (72%). Thus, it cannot be accurately inferred from these results whether U-line triple junctions are actually the preferred void nucleation sites. A more statistically sound analysis based on a much larger number of triple junctions is required to examine this aspect.

**Figure 15** SEM micrograph of one of the larger wedge-shaped cavities observed at a triple junction. The lines represent the three intersecting grain boundaries, as determined by EBSD pattern changes.
6. DISCUSSION

6.1 Grain Boundary Cavitation

6.1.1 Brandon's Criterion

According to the findings presented in the section 5.2.1 (Brandon's criterion), the following statements can be made:

1. Cavitation occurs primarily along paths of random boundaries;
2. Low angle ($\Sigma 1$) and twin ($\Sigma 3$) boundaries are more resistant than random and $\Sigma 5 - 29b$ boundaries; and
3. No cavitation selectivity was observed between random and $\Sigma 5 - 29b$ CSL boundaries.

In the section 1.2, it has been suggested that grain boundary diffusion and/or grain boundary sliding can be instrumental in causing intergranular creep cavitation. It was also mentioned in section 1.3.1 that there is evidence showing that low $\Sigma$ CSL boundaries are more resistant to grain boundary sliding$^{16,17}$ and grain boundary diffusion$^{18,19}$. Therefore, it follows that these "special" boundaries are expected to be more resistant to intergranular creep cavitation. This would then explain why a stronger random cavitated grain boundary component, rather than a stronger low $\Sigma$ CSL cavitated grain boundary component, was observed for all samples. Furthermore, the observation that the overall GBCD was different than the distribution of different cavitated grain boundary types indicated that the preceding observation was not a result of the number of each type of boundaries present. In other words, the findings illustrate that there exists a grain boundary structural influence on intergranular creep cavitation of OFHC copper crept at slightly elevated temperatures.
The observation that, for both random and $\Sigma 5 - 29$ b CSL grain boundaries, the cavitated boundary frequency was greater than the corresponding component for the overall GBCD suggests that there is a lack of cavitation selectivity between these two boundary groups. This seems to contradict expectations (see sections 1.3.1 and 2.2.1) because it implies that $\Sigma 5 - 29$ b CSL boundaries may be just as strong or even weaker than random grain boundaries. However, it should be noted that the resistance to creep cavitation of a grain boundary cannot be inferred solely on the basis that cavitation was detected on that boundary. Furthermore, since no boundary is indestructible, it is entirely possible that the creep test conditions (stress and temperature) used in the present work may have been too severe for cavitation selectivity to be revealed. This is supported by the "locations" of the creep tests conducted by OHT on the Ashby map (see Figure 4) which indicates the tests were conducted in the power-law creep regime. In other words, there may be a threshold condition above which cavitation selectivity disappears. This suggestion is analogous to corrosion experiments conducted by Palumbo and Aust, where it was observed that at a sufficiently high overpotential, all boundaries corroded regardless of "character" or type.

6.1.2 The Palumbo-Aust Criterion

The lack of cavitation selectivity discussed in the previous section between random and $\Sigma 5 - 29$ b CSL boundaries may, however, be simply due to the Brandon's criterion being not restrictive enough. As mentioned in section 2.2.2, grain boundaries considered low $\Sigma$ CSL under one criterion, may be considered random under another. This may explain anomalous findings (including those of this thesis), which suggest that low $\Sigma$ CSL may be
weaker or just as resistant to various adverse conditions as random boundaries. Evidence of this has been recently been provided by Pan et al.\textsuperscript{36} for Alloy X-750. They observed that cracked CSL ($\Sigma 5 - 49$) boundaries were classified as random boundaries under the more restrictive Palumbo-Aust criterion.

In this thesis, the analysis performed using the Palumbo-Aust criterion illustrates that for all samples, virtually all the cavitated boundaries were found to be random grain boundaries. Note that this particular analysis was performed using the exact same cavities (actually crystallographic data) as those used for the Brandon’s criterion analysis. This suggests that most of the cavitated low $\Sigma$ CSL ($\Sigma 3 - 29b$) boundaries classified using Brandon’s criterion are considered random by the Palumbo-Aust criterion. This demonstrates the need for caution when selecting a particular deviation criterion to analyze grain boundary characterization data.

In the previous section, it was shown that no cavitation selectivity between random and $\Sigma 5 - 29b$ CSL boundaries was observed when applying Brandon’s criterion. However, using Palumbo-Aust criterion revealed, for samples 1-6 and 3-6, that other than a few low angle boundaries, all the cavitated grain boundaries were random. Since there were some $\Sigma 5 - 29b$ CSL boundaries characterized in the overall GBCD for both samples 1-6 and 3-6, it can thus be said that there is a possibility that random boundaries are preferred cavitation paths over $\Sigma 5 - 29b$ CSL boundaries. However, this conclusion must be treated with care since the statistical significance is not very high. Only 0.2% of the overall GBCD for samples 1-6 and 3-6 are $\Sigma 5 - 29b$ CSL boundaries which corresponds
to very few boundaries in the total count of typically 500-1000 grain boundaries per OIM run. Clearly, a much better statistical analysis is required to make any unambiguous statements regarding the resistance to cavitation of Σ 5 - 29b CSL boundaries.

One possible explanation for the persistent lack of selectivity for Σ 5 - 29b CSL boundaries in sample 2 could be the actual creep test for this particular sample (see Figure 15 in appended in section 9.1). In Figure 15, it is observed that sample 2 (creep curve No. 5 under OHT's designation) has entered the tertiary creep regime. In contrast, the curves corresponding to samples 1-6 and 3-6 (curves 2 and 7 respectively) show that these samples have not yet entered the tertiary creep stage. This alludes to the possibility of the creep conditions for sample 2 being too severe which may have contributed to the lack of selectivity.

Thus, from the analyses of both this section and the preceding section, it can be said that there exists a grain boundary structural influence on intergranular creep cavitation of OFHC copper. Furthermore, both analyses indicate that low Σ CSL grain boundaries may be more resistant to intergranular creep cavitation than random grain boundaries. The most cavity resistant grain boundaries are the low angle (Σ 1) and twin (Σ 3) boundaries.
6.2 Triple Junction Cavitation

From the results of the analysis of cavitation found in connection with triple junctions, the following statements can be made:

1. Fewer I-lines than expected from the overall I-line frequency were associated with one or more boundaries showing cavitation.

2. No correlation between triple junction character and cavity nucleation could be made.

The first finding indicates that there may be some correlation between cavity nucleation and growth, as well as crack arrest and the character of triple junctions. However, it is difficult to assess these correlations in more detail using the data available from this thesis.

In order to establish with a high degree of certainty which type of triple junctions are preferential cavity nucleation sites and which type arrests cavity growth, experimental work should be performed with a much larger grain size than that determined for the material studied in this thesis. This would allow one to study grain boundary and triple junction effects in the same area on the sample. The results should be analyzed as a function of creep test time. And prior to testing, the character of boundaries and triple junctions found in the set area should be also determined, perhaps with an OIM system. This would allow for comparison of cavity nucleation and growth in the same area as the creep tests progresses.
The lack of selectivity observed for the wedge-shaped cavities found at triple junctions is akin to the lack of selectivity observed for grain boundaries between random and $\Sigma 5$ - 29b boundaries. Again one possible reason could be that the stress levels at which the creep tests were conducted were too high. This was seen in the Ashby deformation map (Figure 4). Also, the statistical confidence (11 U-lines out of 14 triple junctions) of the analysis is not as high as one would like it to be. Unfortunately, intergranular creep cavitation in the samples had progressed into a more advanced stage where cavity growth and coalescence made it difficult to ascertain the role of the triple junctions.

However, the role of triple junctions in creep deformation should not be ignored. This is due to the potential application of triple junction design and control as a means of improving material resistance to intergranular creep cavitation. This has been hinted at in this thesis (point 1 of this discussion) and has also been suggested by work performed by Randle\textsuperscript{13}. Evidence presented in Randle's work suggested that I-lines were able to arrest crack propagation. This finding suggests that enhancing the frequency of I-lines could possibly improve the resistance of OFHC copper to intergranular creep cavitation.

### 6.3 Texture Effects

From the overall GBCD and triple junction distributions observed for the samples used in this thesis, the following statements can be made:

1. Relatively high frequencies of $\Sigma 1$ grain boundaries were observed
2. The overall I-line frequencies of all three samples were on average about 25%.

Point 1 was observed through a comparison of the average overall GBCD for the three samples used in this study, with that of a sample with random crystal orientations, as for example listed by Aust et al.\textsuperscript{47}. Table 9 is a comparison of these two distributions. Furthermore, the I-line frequency in a sample with random crystal orientations as suggested by Doni et al.\textsuperscript{48}, is only 4%. This is significantly lower than the average I-line frequency (25%) for all samples studied in this thesis.

Table 9 A comparison of the overall GBCD with the GBCD of a sample with random crystal orientations

<table>
<thead>
<tr>
<th></th>
<th>Random Boundaries (%)</th>
<th>Σ 1 Boundaries (%)</th>
<th>Σ 3 Boundaries (%)</th>
<th>Σ 5-29b Boundaries (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Overall GBCD determined</td>
<td>24.8</td>
<td>59.2</td>
<td>12.8</td>
<td>3.2</td>
</tr>
<tr>
<td>Random Crystal Distribution</td>
<td>87.4</td>
<td>2.2</td>
<td>1.8</td>
<td>8.6</td>
</tr>
</tbody>
</table>

A high frequency of low angle boundaries observed in a material is an indication that the material may be highly textured. Crystallographic data from the OIM runs indicated that this was indeed the case as shown in Figures 11 to 14 (in the results section 5.3). The finding that the material studied in this thesis is textured may also explain the high frequency of I-lines found in these creep samples. This assumption is based on work by Doni et al.\textsuperscript{48}, which showed that an increase in fibre texture strength of FCC materials leads to a decrease in U-line content and conversely an increase in the I-line content. The presence of the [111] [200] duplex fibre texture, in the creep samples, is probably the
result of the extrusion process, and can therefore be considered the main reason for the higher frequency of I-lines and the high frequency of low angle (Σ 1) boundaries.
7. **SUMMARY**

Returning to the three requirements for the successful application of grain boundary design and control as stated in section 1.3.2, the findings of this thesis illustrate that: 1) the phenomenon in question in this thesis is intergranular in nature and 2) there exists an influence of grain boundary structure on intergranular creep cavitation of copper crept at slightly elevated temperatures. This structural influence was demonstrated by showing that:

1. Intergranular creep cavitation occurs primarily on random boundaries; and
2. Low angle and twin boundaries are the most intergranular creep cavitation resistant boundaries

In addition, this thesis has also demonstrated the need for caution when selecting a deviation criterion for the analysis of collected grain boundary characterization data.

Thus, the way is paved for others to determine precisely the amount of material improvement required, possibly through grain boundary design and control, in order to bring the intergranular creep cavitation resistance up to a satisfactory level. Achieving this would then fulfill the third and last requirement.

Although structural influence on intergranular creep cavitation has been demonstrated for grain boundaries, more research is required in the area of triple junction structural influence. Of particular concern is the effect of triple junction structure on cavity nucleation.
8. FUTURE WORK

Since this thesis has illustrated that there is grain boundary structure influence on intergranular creep cavitation of OFHC copper, then the logical next step would be to apply grain boundary design and control to engineer the overall grain boundary character distribution of polycrystalline OFHC copper. Creep tests conducted on the engineered material would then enable researchers to determine the third requirement of successful grain boundary design and control (see section 1.3.2). More specifically, in this thesis, since it was illustrated that low angle (Σ 1) and twin (Σ 3) boundaries are the most cavitation resistant grain boundaries, it would be desirable to engineer OFHC copper such that it contains even higher frequencies of occurrence of both these boundaries. Increasing the presence of these two boundaries, may also increase the presence of I-lines which may have a beneficial effect on void nucleation, growth, as well as cavity growth arrest. However, a more statistically sound examination of the role of triple junctions as void nucleation sites should be first conducted.

Although it was suggested that the lack of selectivity observed between random and Σ 5 - 29 b CSL boundaries was a result of creep conditions (stress and temperature) being too severe, this reason still has to be verified. Thus, future creep tests need to be conducted under conditions closer to the actual service conditions which the nuclear waste canisters might encounter.
9. APPENDICES

9.1 Appendix 1: Creep curves

Figure 16 Creep curves for all the OFHC copper samples tested by OHT. Creep curves 2, 5 and 7 correspond to samples 1, 2 and 3 in this thesis respectively. Taken from ref. (7)
9.2 Appendix 2: Values and equations used to determine the positions for the three creep tests on Ashby map

Melting Point of Copper: 1083°C (1356 K)

Young’s Modulus:
(temperature compensated, equation taken from ref. (49))

Tests 1 & 2 (100°C): 1.08*10^5 MPa

Test 3: 1.06*10^5 MPa

Shear Modulus (G):
μ = E / (2 * (1 + ν))
where ν = 0.33

Table 10 Table showing some of the values used to determine the location of the three creep tests on the Ashby Deformation Map

<table>
<thead>
<tr>
<th>Sample</th>
<th>Applied Stress (σₐ) (MPa)</th>
<th>Max Shear Stress (σₛ = 0.5 σₐ) (MPa)</th>
<th>Calculated Shear Modulus (μ) (MPa)</th>
<th>Normalized Shear Stress (σₛ / μ)</th>
<th>Homologous Temperature (T / Tₘ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample 1</td>
<td>52.0</td>
<td>26.0</td>
<td>40602</td>
<td>6.4*10⁻⁴</td>
<td>0.28</td>
</tr>
<tr>
<td>Sample 2</td>
<td>64.5</td>
<td>32.25</td>
<td>40602</td>
<td>7.9*10⁻⁴</td>
<td>0.28</td>
</tr>
<tr>
<td>Sample 3</td>
<td>64.5</td>
<td>32.25</td>
<td>39850</td>
<td>8.0*10⁻⁴</td>
<td>0.31</td>
</tr>
</tbody>
</table>
9.3 Appendix 3: Electropolishing (Electrolyte Composition and Polishing Parameters)

Composition of Struer's D2 solution

250 ml Ortho-Phosphoric Acid
500 ml Distilled water
250 ml Ethanol
2 ml Vogel Sparbeize
50 ml n-Propanol
5 g Urea

Electropolishing Parameters

Table 11 Table listing the electropolishing parameters used.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Time</td>
<td>12 s</td>
</tr>
<tr>
<td>Electrolyte Temperature</td>
<td>21 °C to 25°C</td>
</tr>
<tr>
<td>Voltage</td>
<td>12 V DC Fixed</td>
</tr>
<tr>
<td>Solution Type</td>
<td>D2</td>
</tr>
</tbody>
</table>
9.4 Appendix 4: Reinterpretation of OIM data with a focus on the low angle boundary frequencies

In this thesis, results from the OIM runs (see table 4) indicate that the component of the overall GBCD (for all samples) determined to be low angle (Σ 1) boundaries was on average 59.2%. However, a more detailed analysis of the OIM results reveals that a significant number of the boundaries determined by the OIM software to be low angle (Σ 1) boundaries may instead be artifacts due to deformation (see Figures 17-20, “Σ 1” boundaries are coloured in red). This deformation can be attributed to the extrusion and creep testing processes since no annealing was done on the test specimens before or after creep.

From the maps, it can be seen that increasing the minimum misorientation angle from 2° to 5° decreases the amount of artifacts. Figures 17-20 show OIM maps for sample A-6. However, the trend is similar for all the samples. The overall GBCD was re-determined for the crept samples (1-3) by selecting a minimum misorientation angle limit of 5° for low angle boundaries and manually counting the different types of boundaries intersecting 10 lines. The selection of 5° in this thesis was due to the observation that the angles of misorientation for all the cavitated low angle (Σ 1) boundaries were at least 5°. Manual counting was made possible by highlighting the four groups of different boundary types with different colours as seen in Figure 20 and performed for both the Brandon criterion (equation 5) and the Palumbo-Aust criterion (equation 6). In Figure 20, the low angle (Σ 1) boundaries are red, the twin (Σ 3) boundaries are green, the Σ 5-29b boundaries are
blue and the random boundaries are black. A comparison of the results with the cavitated frequency distributions are shown in Tables 12 and 13.

**Table 12** Table comparing the different cavitated grain boundary type frequencies with the overall GBCD as determined by the manual counting method (Using Brandon’s criterion)

<table>
<thead>
<tr>
<th></th>
<th>Random (%)</th>
<th>Σ 1 (%)</th>
<th>Σ 3 (%)</th>
<th>Σ 5-29b (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Sample 1-6</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cavitated</td>
<td>68.2</td>
<td>0</td>
<td>4.6</td>
<td>27.2</td>
</tr>
<tr>
<td>Non-cavitated</td>
<td>50.9</td>
<td>9.0</td>
<td>35.1</td>
<td>5.0</td>
</tr>
<tr>
<td><strong>Sample 2-6</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cavitated</td>
<td>84.6</td>
<td>4.1</td>
<td>1</td>
<td>10.3</td>
</tr>
<tr>
<td>Non-cavitated</td>
<td>54.5</td>
<td>6.3</td>
<td>34</td>
<td>5.1</td>
</tr>
<tr>
<td><strong>Sample 3-6</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cavitated</td>
<td>88.7</td>
<td>2.4</td>
<td>1.6</td>
<td>7.2</td>
</tr>
<tr>
<td>Non-cavitated</td>
<td>44</td>
<td>5.7</td>
<td>44.7</td>
<td>5.7</td>
</tr>
</tbody>
</table>

**Table 13** Table comparing the different cavitated grain boundary type frequencies with the overall GBCD as determined by the manual counting method (Using the Palumbo-Aust criterion)

<table>
<thead>
<tr>
<th></th>
<th>Random (%)</th>
<th>Σ 1 (%)</th>
<th>Σ 3 (%)</th>
<th>Σ 5-29b (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Sample 1-6</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cavitated</td>
<td>100</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Non-cavitated</td>
<td>71.2</td>
<td>9.0</td>
<td>19.6</td>
<td>0</td>
</tr>
<tr>
<td><strong>Sample 2-6</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cavitated</td>
<td>92.8</td>
<td>4.1</td>
<td>1.0</td>
<td>2.1</td>
</tr>
<tr>
<td>Non-cavitated</td>
<td>72.4</td>
<td>6.3</td>
<td>20.9</td>
<td>0.4</td>
</tr>
<tr>
<td><strong>Sample 3-6</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cavitated</td>
<td>97.6</td>
<td>2.4</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Non-cavitated</td>
<td>68.1</td>
<td>5.7</td>
<td>25.5</td>
<td>0</td>
</tr>
</tbody>
</table>
**Figure 17** Figure showing an OIM map for sample A-6. Low angle boundaries with a minimum misorientation angle of $2^\circ$ are shown in red.

**Figure 18** Figure showing an OIM map for sample A-6. Low angle boundaries with a minimum misorientation angle of $3^\circ$ are shown in red.
Figure 19  Figure showing an OIM map for sample A-6. Low angle boundaries with a minimum misorientation angle of 4° are shown in red.

Figure 20  Figure showing an OIM map for sample A-6. Low angle boundaries with a minimum misorientation angle of 5° are shown in red.
Fortunately for this thesis, the “new” results illustrate that there is no change in the overall conclusions (section 7). However, it is critical that others who use the OIM results from this thesis be made aware that the frequency of low angle boundaries is artificially inflated by deformation. This observation could also be true outside of this thesis. Hence, it was shown that careful interpretation of the OIM results with regards to the low angle boundaries is mandatory, especially for deformed materials.
10. REFERENCES


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