Orientation connectivity and GB networks

• The topological parameters associated with polycrystals—numbers of grains, grain surfaces, edges, and corners—have been studied for many years.

• Stereological techniques (i.e., the reconstruction of 3-D information based on that accrued from 2-D sections) have generally been used to investigate the topological connectivity of grains aggregated in a polycrystal.

• The sectioning planes can be random, which gives a statistical result.

• These topological aspects of microstructure have traditionally been studied separately from crystallographic considerations.

• However, the advent of EBSD allows large regions of microstructure to be accessed in a single section in terms of both the crystallography and areal topology.

• These studies access the way in which grains having various orientations connect together—orientation connectivity.
Another aspect of orientation connectivity is the spatial distribution of orientations with respect to some features of the microstructure; for example, how grain textures relate to grain size or the clustering of grains that are separated by low angle boundaries, where a single cluster is enclosed by high-angle boundaries.

Quantitative cluster structure analysis is carried out using aspects of percolation theory, such as fractal analysis. Examples of specific orientation connectivity topics include the following:

- Grain shape, distribution, and orientation
- “Decision trees” for crack paths throughout the microstructure
- Grain boundary connectivity
- Clustering of orientation elements

Any of these examples can be explored on a single section through the microstructure; if sectioning techniques are employed then 3-D aspects of orientation connectivity can be addressed, which render the data much more powerful.

Other metrics are beginning to be used to assess the connectivity and topology of the grain boundary network.

Percolation theory is relevant to the length of connected intergranular pathways or “clusters” through the microstructure.
A simple approach is to consider that such pathways consist only of boundaries with random geometries.

A GB map from EBSD data can be used to show the evolution of connected random boundaries with processing.
Aspects of orientation connectivity that relate to grain junctions, that is, where more than two grains meet, are often called a “triple line”.

An “addition rule” applies, which predicts the geometry of the third boundary from the relationship:

\[ M_1 M_2 M_3 = I \]

where \( M_{1-3} \) are the misorientation matrices of three boundaries at a common junction and \( I \) is the identity matrix.

This rule has the most significant consequences for conjoining CSL boundaries since they share a common misorientation axis; the sum of two of the misorientation angles gives the third multiplied by a common factor, and the product or quotient of two of the \( \Sigma \) values gives the third.

\[ 60^\circ / \langle 111 \rangle - 21.8^\circ / \langle 111 \rangle = 38.2^\circ / \langle 111 \rangle \]

that is, \( \Sigma 3 = \Sigma 21a = \Sigma 7 \)

\[ x \cdot y = k^2 \cdot z \]

where \( k \) is a common factor of \( x, y, z \) (CSL boundaries).
The interest in grain junctions from a practical point of view is that any interfacial propagation phenomenon (diffusion, corrosion, cracking, etc.) is controlled by the juxtaposition of boundaries at grain junctions.

The phenomenon will only be likely to propagate along nonspecial boundaries; therefore, it is pertinent to categorize grain junctions in terms of the combinations of special/nonspecial types.

In recent years, statistics on triple junctions have begun to appear in reports alongside grain boundary proportions.
Color code: [ Σ3 – red; Σ9 – blue; Σ27 – green; other HAGBs – black]
Corrosion performances of various boundaries

Corrosion behaviors of $\Sigma 3^n$ ($n = 1, 2, 3$) boundaries and random HABs (denoted by the symbol ‘R’) in type 304L stainless steel
Corrosion performances of various boundaries

Corrosion behaviors of $\Sigma 5$ boundaries in type 304L stainless steel
Grain Boundary Engineering

• Grain Boundary Engineering (GBE) is the practice of obtaining microstructures with a high fraction of boundaries with desirable properties.

• In general, desirable properties are associated with boundaries that have simple, low energy structures.

• Such low energy structures are, in turn, associated with CSL boundaries.

• GBE generally consists of repeated cycles of deformation and annealing, chosen so as to generate large fractions of “special boundaries” and avoid development of strong recrystallization textures.

• GBE is largely confined at present to fcc metallic systems such as stainless steel, nickel alloys, Pb, Cu etc.

• GBE is mostly linked to low \( \Sigma (\leq 29) \) boundaries. Among these \( \Sigma 3 \) (twin boundaries) are mostly low low energy and exploited to achieve GBE microstructure.
Modification of grain boundary character by GBE

- To increase the fraction of low $\Sigma$ ($\leq 29$) coincidence site lattice (CSL) boundaries
  - Low $\Sigma$ ($\leq 29$) CSL boundaries are often referred to as ‘special boundaries’

- To disrupt the random high angle grain boundaries (HAGBs) connectivity
Annealing twins

• Annealing twins are formed as a consequence of growth accidents during the recrystallisation of deformed cubic-close packed metals such as alpha-brass, copper, nickel and austenitic iron.

• Annealing twins should be distinguished from mechanical twins.

• There is a lot of strain energy associated with the formation of a mechanical twin, whose shape is determined strictly by the need to minimise strain energy.

• This contrasts with annealing twins where the shape is determined by the need to minimise interfacial energy.

• Mechanical twins tend to be lenticular, i.e., lens shaped with sharp edges, since this reduces the long range elastic strains.

• Annealing twins, are not pointed since there is no deformation associated with their formation.
Annealing twins were seen in gold as early as 1897. A great deal of empirical evidence suggests that the important factors determining the frequency with which they occur are:

- grain size;
- temperature and time of annealing;
- grain boundary velocity;
- grain boundary energy;
- twin boundary or stacking fault energy;
- crystallographic texture;
- degree of prior deformation;
- presence of inclusions.

A large grain boundary velocity favours the formation of annealing twins because growth accidents, which are responsible for annealing twin formation, are then more frequent.

A low stacking fault energy also favours annealing twins since growth accidents are easier to tolerate.
Annealing twins

Shows recrystallised grains which show uniform contrast because they are relatively free of dislocations, surrounded by a deformed matrix which has a high dislocation density. The recrystallised grain contains annealing twins (parallel bands with different contrast. The steps at the top left-hand corner are simply steps in annealing twin boundaries.
Multiple Twinning in a real microstructure!!

\[ \Sigma 3 \times \Sigma 3 = \Sigma 9 \]
\[ \Sigma 3 \times \Sigma 9 = \Sigma 27 \]
\[ \Sigma 3 \times \Sigma 9 = \Sigma 3 \]

Color code: [ \( \Sigma 3 \) – red; \( \Sigma 9 \) – blue; \( \Sigma 27 \) – green; other HAGBs – black]
Methodology to achieve GBE microstructure

Applying magnetic field during annealing

When the difference in the magnetic susceptibility of one phase is greater than others, the driving force originating from the difference of the magnetization energy causes the migration of the interphase boundary.

Applying mechanical stresses during annealing

Externally applied mechanical stress field can drastically change grain growth as well as recrystallization kinetics and can strongly influence the microstructure evolution.

Combining laser surface melting with annealing treatment

Owing to the rapid cooling rate following laser surface melting, there exists certain strain in the molten zone after solidification.

Thermo-mechanical processing (TMP)
Methodology to achieve GBE microstructure

✓ Amongst all these approaches, TMP is found to be most effective and widely employed

✓ There is however no fixed TMP schedule that can be applied to achieve GBE microstructure in all materials.

✓ This could be attributed to the large number of variables associated with the TMP process, such as
  - The material properties (particularly SFE)
  - The starting microstructure
  - The mode (compression, tension or rolling)
  - Extent of deformation employed
  - The annealing time and temperature
GBE in alloy 617 by Iterative thermomechanical processing

As-Received

1st Iteration
15% deformation 1373 K 1h

2nd Iteration
15% deformation 1373 K 1h
+ 10% deformation 1273K 0.5h

3rd Iteration
15% deformation 1373 K 1h
+ 10% deformation 1273K 0.5h
+ 5% deformation 1273K 0.5h
Evolution of $\Sigma^{n}$ (n = 1,2,3) boundaries and the grain size as a function of iterations in alloy 617
GBE in alloy 617......Implication on Hot corrosion

Exposed to salt-mixture of (75%Na$_2$SO$_4$ + 20%NaCl + 5%V$_2$O$_5$) at 1273K for 24h

As-Received

Substantially damaged

GBE

Only top layer is damaged

SEM images of cross-section showing the intergranular damage due to hot corrosion
GBE in alloy 617......Implication on Hot corrosion

EDS elemental map of cross section of oxide layer showing distribution of Cr and oxygen on the oxide scale that was formed on the surface of AR specimen after hot corrosion
Segregation of elements in AR specimen during hot corrosion

Segregation of Ni, Mo, Cobalt (not shown here) and S at GBs occur – It indicates penetration of S and eventual segregation of S at the random HAGBs.

Segregation of Mo, Co and Ni along with S at random HAGBs gives an indication of formation of Mo, Co, Ni mixed sulphide.

Depletion of Cr at GBs – Cr moves upward through random HAGBs and form chromium oxide at the surface

The coexistence of Al and O suggest the formation of $\text{Al}_2\text{O}_3$
Segregation of elements in GBE specimen during hot corrosion

The GBE specimen shows a lesser penetration of S and O\textsubscript{2} into the alloy due to the discontinuous network of random HAGBs.

The low \Sigma\text{CSL} GBs appear to be resistant to the diffusion of S and thereby prevent its percolation deeper into the alloy which eventually protects the core of the alloy from hot corrosion attack.

As a result, the enrichment of Mo, S, Co, Ni and depletion of Cr in GBE specimen is limited only to a few \textmu m only.
GBE and grain boundary sliding

- Random boundaries (R) could easily slide and preferentially fracture
- Random boundaries are fast path for atomic diffusion whereas low-energy boundaries are not
- This leads to structure-dependent diffusion-controlled intergranular cavitation and fracture during plastic deformation at high temperatures

Structure-dependent intergranular creep fracture in Fe–0.8 at% Sn alloy crept at 973K and 29.4MPa
Improvement in creep strength through GBE

- Low-\(\Sigma\) boundary act as a more effective barrier to dislocation motion in comparison with the random boundary.

- Grain boundary sliding is much more difficult at low-\(\Sigma\) boundary than random boundary.

The creep curves obtained by creep test: (a) at 1073K for 24 h in air under stress of 14MPa, and (b) at 1200K for 18 h in air under stress of 10MPa or rapidly solidified and annealed Ni–40 at.% Fe alloy specimens with different frequencies of low-\(\Sigma\) coincidence boundaries and grain sizes.
**GBE to increase oxidation resistance**

- Weight gain vs. exposure time curves clearly indicate that an increase in the fraction of CSL boundaries leads to a decrease in the oxidation rate.

This was attributed to slower interfacial diffusivity of oxygen along CSL boundaries to form $\text{Al}_2\text{O}_3$.

Oxidation kinetics of three IN718 specimens with various fractions of CSL grain boundaries during exposure at 1123 K to air.
GBE to minimize intergranular segregation

SIMS boron images from (a) AR alloy 304 and (b) GBE alloy 304, heat-treated for 2.5 min at 1000°C

Low $\Sigma$ CSL
$\sim 47\%$

Low $\Sigma$ CSL
$\sim 62\%$
Radiation induced segregation (RIS) at boundaries

✓ Point defects migrate to defect sinks such as grain boundaries and surfaces during irradiation. The persistent flux of point defects to the sinks gives rise to the phenomenon of radiation-induced segregation (RIS).

✓ The vacancy flux $J_V$ to the sink essentially corresponds to the flux of solute atoms $J_A$ and $J_B$ away from the sink with $J_V = J_A + J_B$. If both the alloy components A and B diffuse at the same rate, there will be no net enrichment or depletion of any element at the sinks. However, if $J_A > J_B$, A gets depleted at the sink.

✓ In austenitic stainless steel, the segregation arises because elemental diffusivities are different, with $D_{Cr} > D_{Fe} > D_{Ni}$

✓ So, Ni segregates and Cr depleted at GBs due to RIS
Radiation induced segregation (RIS) at boundaries

RIS at two different grain boundaries after electron irradiation to 3 dpa at 723 K: (a) a small angle tilt grain boundary (θ = 3.5°) (b) a random grain boundary (θ = 60°); solid lines are theoretical predictions and unfilled characters are experimental data.
GBE to minimize radiation induced segregation

Fe-15Cr-20Ni, Electron Irrad., 2e-3dpa/s, 3dpa, 623K

[SUS304L, Proton Irrad., 1e-6dpa/s, 1dpa, 723K]

<110> tilt angle dependence of RIS at grain boundaries in electron-irradiated Fe–15Cr–20Ni alloys

<210> tilt angle dependence of Cr segregation at grain boundaries in proton-irradiated type 304L stainless steels
Nano twinned Cu obtained by pulsed electrodeposition
Nano twinned Cu has high strength and ductility and very good conductivity.