CHAPTER 8

SUB-GRAIN BOUNDARY IN Li₂CO₃ SINGLE CRYSTALS
8.1. Introduction:

During the growth process of materials, sometimes many small interlocking crystals or grains may be formed. Each of these crystallites is misoriented with respect to neighbours to a greater or lesser degree. Often these interlocking crystallites are called grains and the regions between crystallites are called grain boundary.

8.1.1. Low angle grain boundary:

When the angle between adjacent crystallites is small, the resultant low angle grain boundary consists of an array of dislocations (1, 2). Fig. 8.1(a) shows the structures of two adjacent grains and they are tilted by a few degrees relative to each other. When the tilt is not too large, these grains (Fig. 8.1(a)) can be joined as shown in the Fig. 8.1(b). It can be seen that it consists of a series of edge dislocations. Such an arrangement of edge dislocations defines a grain boundary separating two regions of the crystals that differ in orientation by an angle.

\[ \theta = \tan^{-1} \frac{b}{D} \]  

...8.1

where 'D' is the distance between dislocations and 'b' is a Burger's vector. This equation 8.1 is valid only for small angle of rotation. As the author already mentioned in chapter 7, in general grain boundaries can be a mixture of the tilt and twist type in which case they must contain several sets of different edge and screw dislocations.
FIG. 8.1  (a) STRUCTURE OF TWO ADJACENT GRAINS TILTED BY FEW DEGREES RELATIVE TO EACH OTHER.

(b) FORMATION OF EDGE DISLOCATION WHEN $\theta$ IS NOT TOO LARGE.
At very small values of $\theta$ the distance between dislocations $D$ is very large and the grain boundary energy $\gamma$ is approximately proportional to the density of dislocations in the boundary $(1/D)$ i.e.

$$\gamma \propto \theta \quad \ldots 8.2$$

However as $\theta$ increases the strain fields of the dislocations progressively cancel out so that $\gamma$ increases at a decreasing rate as shown in Fig. 8.2. In general when $\theta$ exceeds $10-15^\circ$ the dislocation spacing is so small that the dislocation cores overlap and it is then impossible to physi- cally identify the individual dislocations (Fig. 8.3). At this stage the grain-boundary energy is almost independent of misorientation (Fig. 8.2).

8.1.2. Random large angle boundary:

When $\theta > 10-15^\circ$ the boundary is known as large-angle grain boundary. The angle of rotation is

$$b_D = 2 \sin \theta/2 \quad \ldots 8.3$$

Analysis of grain boundaries with large misorientation angles is more complicated. Large angle boundaries contain large area of poor fit and have a relatively open structure. The bonds between the atoms are broken or highly distorted and consequently the boundary is associated with a relatively high energy. In low angle boundaries, however, the most of the atoms fit very well into both lattices so that there is
FIG. 8.2 VARIATION OF GRAIN BOUNDARY ENERGY WITH MISORIENTATION

FIG. 8.3 DISORDERED GRAIN BOUNDARY STRUCTURE.
very little free volume and the interatomic bonds are only slightly distorted.

8.1.3. Special large angle boundaries:

There are some special large angle boundaries which have significantly lower energies than the random boundaries. These boundaries only occur when two misoriented single crystal sections are identical but are joined together in such a way that the boundary constitutes a reflection plane of symmetry, the pair constitutes a twin. If the twin boundary is parallel to the twinning plane, the atoms in the boundary fit perfectly into both grains. The result is coherent twin boundary. Because the atoms in the boundary are essentially in undistorted positions, the energy of a coherent twin boundary is extremely low in comparison to the energy of a random large angle boundary.

When the twin boundary does not lie exactly parallel to the twinning plane, the atoms do not fit perfectly into each grain and the boundary energy is much higher. This is known as an incoherent twin boundary. The energy of a twin boundary is therefore very sensitive to the orientation of the boundary plane.

The relationships of equations 8.1 and 8.2 give a physical meaning to the dependence of the structure and properties of
the boundary on the misorientation angle of grains in a dislocation model. It turns out that the dislocation density depends on the misorientation angle of grains.

8.1.4. Sub-boundary:

Within the grains of a single crystal so called sub-boundaries divide the crystalline grains into sub-grains which are slightly misoriented. The two misoriented (small angle) grains in a single crystal meeting at the boundary is partially relieved by an elastic deformation extending over an area of several interatomic spacings wide. When the misoriented grains join at the grain boundary and form a large crystal, the energy of a crystal containing many edge dislocations is lowered because the dislocation stacks above each other in a plane. Such a plane of dislocation is sometimes called a dislocation wall and is very similar to the small angle boundary. These walls are frequently found to form, when a plastically deformed crystal is annealed. Phonons interact with the edge dislocations and provide the dislocation lines with the energy necessary to migrate through the crystal and to collect in walls, forming sub-boundaries frequently called polygonization boundaries.

Guinier (3) has reported the sub boundaries in crystals. According to him the sub boundaries are of irregular, discontinuous or continuous character. The sub boundary has a
misfit greater than a twin boundary and less than an ordinary boundary and it will stop at the grain boundaries.

The production of sub boundaries during the deformation itself has been explained by McLean (4) as the result of local rearrangement of the dislocations in slip bands.

In high temperature growth, in the presence of thermal stress the material may be strained and hence its free energy is enhanced over that in the stress-free state. This situation is one of the thermodynamically unstable equilibriums. The material tries to return to a state of smaller free energy. This is in general only possible at elevated temperatures where thermally activated processes can help in this tendency. A suitable annealing removes the internal strain, so that elastic energy of the material is relieved. During this process the dislocations are arranged in the form of dislocation walls.

Cottrell (5) has reported that when the strained material is on annealing, the dislocations leave their glide planes by climb and annihilate each other and then arrange themselves in the form of sub-boundaries. Amelinckx (6, 7) has studied the geometrical features of sub-boundaries in annealed alkali halide single crystals in detail. He has observed sub-boundary consisting of parallel lines, square and hexagonal networks.
The dislocation patterns observed on pure copper and 0.05 and 0.10 at % aluminium doped copper single crystals grown from the melt has been studied by etch pit technique by Watanabe et al (8). In pure copper single crystals, they have observed sub-boundaries with randomly distributed dislocation etch pits. In this crystal sub-boundaries are arranged as arrays of triangular etch pits. He has also observed sub-boundaries in 0.10 at % aluminium doped copper single crystals which is not present in 0.05 at % of aluminium doped copper single crystals. Hildebrand (9) also observed sub-boundaries in copper single crystals when the annealed crystals were etched.

Inoue et al (10) showed that there was a remarkable tendency for dislocations to rearrange into a network of sub-boundaries in melt-grown Cu single crystals when the random dislocation density exceeded a certain critical value, presumably \( \Xi = 1 \times 10^5 / \text{cm}^2 \).

Barthel et al (11) have studied the concentration dependence of Ir distribution and dislocation structures of Mo-Ir single crystals. They have observed dislocation etch pits and sub-boundaries (consisting of rows of etch pits) on (010) longitudinal section of a crystal with cellular structure and the Ir concentration was 1.5 at %.
In fact, the discovery of the phenomenon of polygonization and the study of the structure and properties of sub-boundaries help considerably to widen our concept of inter-crystalline boundaries.

In the present chapter the author discusses the sub-boundaries observed on (002) cleavages of Li$_2$CO$_3$ single crystals by etching technique.

8.2. Experimental results:
8.2.1. Etching of isolated cleavages:

Freshly cleaved (002) faces of Li$_2$CO$_3$ single crystals are etched with $2\%$ citric acid for 2 min and $3\frac{1}{2}$ min. These etched surfaces are scanned in scanning electron microscope (Cambridge stereoscan Model S-150 and operating voltage 20 KV) after sputtering the etched surfaces with gold and are shown in Figs. 8.4 and 8.5. The following points merit discussion.

i) Arrays of etch pits are observed along with the micropits.

ii) Arrays of etch pits having non-uniform spacing (marked 'N'), terminating (marked 'D') as well as curved ones (marked 'C') are predominant.

iii) They are not crystallographically oriented since they are curved (marked 'C' in Figs. 8.4 and 8.5) and

iv) Within the arrays of etch pits, reveals a large pit enclosing several pits (marked N' in the array N).
Fig. 8.4:  SEM photomicrograph revealing different types of arrays of etch pits (x 570)

Fig. 8.5:  SEM photomicrograph revealing curved and non-uniformly spaced arrays of etch pits (x 595)
8.2.2. Successive etching of isolated cleavage having arrays:

In order to investigate the nature of arrays, the author has studied these arrays by successive etching. Figs. 8.6(a), 8.6(b), 8.6(c) and 8.6(d) are the photomicrographs of the etch patterns produced on etching the isolated cleavage having arrays successively with 2% citric acid for 3 min, 5 min, 12 min and 20 min, respectively. The following points merit discussion.

i) Large number of randomly distributed micropits disappear on successive etching and re-appear on further etching at different sites.

ii) The distribution of etch pits along the two arrays (marked 'A' and 'B' in Fig. 8.6(a)) is different.

iii) On successive etching, the number of etch pits comprising arrays decreases.

iv) On prolonged etching, the array marked 'A' vanishes first, whereas the array 'B' is observed to vanish on further prolonged etching.
Figs. 8.6(a) to 8.6(d). Etch patterns on successive etching of the same region etched in 2% citric acid for 3 min, 5 min, 12 min and 20 min respectively (x 415)

Figs. 8.7(a) and 8.7(b). Etch patterns of a matched cleavage pair etched in 2% citric acid for 3½ min and 2 min respectively (x 415)
8.2.3. Etching of matched cleavage pair:

In order to see whether these arrays represent the arrays of dislocations, a matched cleavage pair is etched with 2% citric acid for different periods. Figs. 8.7(a) and 8.7(b) are the etch patterns produced on etching matched face for 3½ min and 2 min respectively. Inspite of etching for different periods, the exact correspondence of two arrays of etch pits is not lost.

8.2.4. Etch pits density:

The etch pit densities of pure single crystals having isolated etch pits without arrays as well as with arrays and 1% K₂CO₃ doped single crystals are measured. The measured etch pit densities, without taking into account the randomly distributed micropits, on (002) cleavages of pure crystal (Fig. 8.8) and doped crystal (Fig. 4.3(b)) both without arrays as well as with arrays of etch pits (Figs. 8.4 to 8.7) observed on cleavages of pure crystal are shown in Table 8.1. From this table it is clear that the densities of etch pits calculated on pure and doped cleavages without arrays are of the order $10^4$ and $10^5$ etch pits per cm$^2$ and the calculated etch pit densities in crystal region containing dislocation arrays are of the order of $10^6$ to $10^7$ etch pits per cm$^2$ respectively.
Fig. 8.8. : Etch pattern on (002) cleavage of undoped crystal etched in 2% citric acid for 3 min (x 455)

Fig. 8.9. : Etch pattern of an annealed crystal (annealing temperature 400°C for 10 h) etched in 2% citric acid for 1 min (x 360)

Fig. 8.10. : Etch pattern of an annealed crystal (annealing temperature 550°C 10 h) etched in 2% citric acid for 1 min (x 350)

Fig. 8.11. : Etch pattern of an annealed crystal (annealing temperature 550°C for 30 h) etched in 2% citric acid for 3 min (x 350)

Figs. 8.12 and 8.13. : Etch patterns on successive etching of the same region of Fig. 8.11 etched in 2% citric acid for 5 min and 10 min respectively (x 350)
Table 3.1

Distribution of dislocations on (002) cleavages of pure and doped Li$_2$CO$_3$ single crystals.

<table>
<thead>
<tr>
<th>Li$_2$CO$_3$ single crystals</th>
<th>Dislocation distribution</th>
<th>Dislocation density</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure</td>
<td>Isolated pits (Fig. 8.8)</td>
<td>(2-3) x 10$^4$ pits cm$^{-2}$</td>
</tr>
<tr>
<td>Impure (1% K$_2$CO$_3$ doped)</td>
<td>Isolated pits (Fig. 4.3(b))</td>
<td>(1-1.2) x 10$^5$ pits cm$^{-2}$</td>
</tr>
<tr>
<td>Pure</td>
<td>Arrays comprising sub-boundaries (Figs. 8.4 - 8.7)</td>
<td>1.1 x 10$^6$ - 1.5 x 10$^7$ pits cm$^{-2}$</td>
</tr>
</tbody>
</table>
8.2.5. The role of annealing:

In order to investigate the role of annealing on the arrangement of dislocations in the formation of arrays, the author has annealed the crystals at different temperatures and the etch patterns are studied.

First the crystal is annealed up to 300°C for 10 h. Only isolated triangular etch pits are observed. Secondly the crystal is annealed at 400°C for 10 h and then the freshly cleaved cleavage is etched with 2% citric acid for 1 min. It is interesting to report that the individual isolated etch pits are arranging in the form of an array as shown in the Fig. 8.9. Thirdly the crystals are annealed at 550°C for 10 h and 30 h and (002) cleavages of these crystals are etched with 2% citric acid for 1 min and 3 min and the etch patterns are shown in Figs. 8.10 and 8.11 respectively. When the crystal is annealed at 550°C for 10 h, the formation of arrays are close to each other along with the isolated etch pits (Fig. 8.10). But when the annealing time is 30 h, the isolated triangular etch pits are arranged in the form of a single array (Fig. 8.11). On successive etching of the same region of Fig. 8.11 for 5 min and 8 min the number of etch pits along the array decreases and finally disappears (Figs. 8.12 and 8.13).
8.3. Discussion:

The enlargement of arrays of etch pits on successive etching and the exact correspondence of arrays on match faces inspite of etching for different periods suggest that the arrays of etch pits formed represent the arrays of dislocations in the crystals. The variation of etch pit density in the arrays on successive etching and its disappearance can be explained on the basis that the dislocations are of the threading type ( \( \bar{\mathbf{U}} \)) as shown in the schematic diagram (Fig. 8.14) by the author. The dark circle (•), marked in the schematic diagram (Fig. 8.14) indicates the sites of etch pits formation along the arrays on the cleavage. The decrease in the density of etch pits along the array marked A and B in Fig. 8.6(a) on successive etching is clear from the decrease in the number of dark circles. That the dislocations are of threading type as shown in the schematic diagram in Fig. 8.14. This is in excellent agreement with the earlier findings of the author (12).

It is well known that the low angle tilt boundary is an array of parallel edge dislocations with uniform spacing (1, 2, 13-15). A large pit enclosing in itself many pits of the array (pit \( M' \) in the array \( N \) of Fig. 8.4) reveals that the dislocations comprising the array are of different types having different Burgers vectors. The non-uniformity in the spacing of consecutive pits (marked \( N \) in Figs. 8.4 and 8.5) and the disappearance of arrays on prolonged etching (Figs. 8.6(a),
FIG. 8.14 SCHEMATIC DIAGRAM SHOWING ARRAY OF THREADING TYPE OF DISLOCATIONS.
8.6(b), 8.6(c) and 8.6(d)) support the view that the arrays of etch pits reported in the present work do not reveal low angle grain boundaries as the dislocations are of different character. As the observed arrays of etch pits are curved (marked 'C' in the Figs. 8.4 and 8.5) and terminating (marked 'D' in Fig. 8.4) they may not reveal slip bands, as they are not crystallographically oriented. Harada (16) has observed crystallographically oriented edge and screw slip bands lying in the <110> and <100> directions etching on (100) cleavage planes of MgO single crystals. The arrays of etch pits meaning thereby the arrays of dislocations are neither low-angle grain boundaries nor slip bands. The arrays are forming when the crystals are annealed at high temperature (Fig. 8.11). It is concluded that the arrays of dislocations discussed here represent sub-boundaries' comprising dislocations formed due to high temperature annealing resulting in the decrease of the elastic energy content of the crystal on the arrangement of dislocations in walls as reported by Van Buuren (17).

As Li₂CO₃ single crystals are grown by floating zone technique at the temperature of 735°C, high temperature annealing might have introduced localized thermal stresses in the crystal. During the high temperature annealing, the distribution of thermal stresses may be of two kinds. If the distribution of thermal stresses are uniform and small, it may give rise to superficial defects like point defects as evidenced by
the disappearance and re-appearance of scattered micropits at newer sites on successive etching. This kind of micro etch pits are seen in all the photomicrographs of the etch patterns of the chapters 6 to 9. On the other hand the localized deformation caused due to the larger thermal stresses concentrated at some regions, may give rise to the arrangement of dislocations in walls (dislocation density of etch pits of the order of $10^6$ or more), thus favouring the formation of sub-boundaries on (002) cleavages of Li$_2$CO$_3$ single crystals, reported by the author in the present chapter (18).

8.4. Conclusion:

From the above observations and results it may be concluded that the etching technique employed in the present investigations, though simple in operation, is a powerful tool, in revealing the nature of dislocations, dislocation content, grain boundaries, twin boundaries and sub-boundaries formed due to the high temperature annealing of the crystal during growth.
References:

18. Raju, K.S., Palaniswamy, M., Ramasamy, P. and Laddha, G.S.,