Section 4

Grain Boundary Fusion in Polycrystals.

During the course of experiments on annealing of tin polycrystals (vide section 5) in the neighbourhood of melting point, grain boundaries were found to melt earlier than the rest of the matrix. When tin polycrystals were heated to melting point maintaining a temperature gradient, the boundaries appeared as preferentially melted grooves (Fig. 49, X 55). Such preferential melting of boundaries is due to the depression of melting point at those sites. Though there is considerable evidence in literature for its occurrence, the phenomenon has not been satisfactorily explained so far.

Chaudron, Lacombe and Yannacquis (1948) recorded preferential melting of boundaries in case of aluminium. Berghezen, Lacombe, and Chaudron (1950) showed that similar behaviour of boundaries in Al-In alloy was due to the presence of a greater concentration of In at those sites.
It was supported by the work of Montariol, Albert, and Chaudron (1953) and Boullanger (1954). Whereas the former workers used autographic techniques, the latter explained it on the basis of studies of elastic modulus and internal friction phenomena in Al near its melting point.

However, earlier to these workers, Chalmers (1940) determined the depression in m.p. at the boundaries in high purity tin bicrystals (99.98% to 99.99% purity). The depression in m.p. was evaluated by finding the temperatures at which the bicrystals separated under stress and the crystals melted. The temperatures were measured within an accuracy of 0.005°C with a tinsley potentiometer. The temperature at which the crystals separated was found to be independent of the stress in the range of 1000 g.wt/cm² to 3000 g.wt/cm² and the rate of heating. The values of depression in m.p. for various boundaries are given in Table 2.
Table 2

<table>
<thead>
<tr>
<th>boundary angles in degrees</th>
<th>14</th>
<th>26</th>
<th>45</th>
<th>59</th>
<th>70</th>
<th>80</th>
<th>85</th>
</tr>
</thead>
<tbody>
<tr>
<td>temp. diff. in °C</td>
<td>0.143</td>
<td>0.137</td>
<td>0.137</td>
<td>0.132</td>
<td>0.143</td>
<td>0.148</td>
<td></td>
</tr>
</tbody>
</table>

These results could be explained as due to intercrystalline failure at elevated temperatures except for the fact that depression was independent of applied stress and rate of heating. Normally, temperature at which intercrystalline failure manifests itself is altered by a change in the above quantities. These results, therefore, were attributed to the tensions existing in the neighbourhood of boundaries as a result of lattice distortion.

The near constancy of depression in m.p. observed over a wide range of impurity percentage in experiments of Chalmers is also significant. It seems probable that there are other factors besides impurities responsible for this mechanism. Efforts to correlate it with the excess
Fig. 50. Compressional & Tensional Stresses around a Dislocation.

Large Angle Boundary (after Smoluchowski)

Fig. 50 (a)
grain boundary energy could not succeed, as it was
found that the available energy was not sufficient to
cause the same depression in m.p. over the observed width
of the boundary. The suggestion of Chalmers that melting
is due to tensions existing in the vicinity of boundary
seems more probable.

**Depression of m.p. at dislocation.**

An effort is made here to evaluate the depression
in m.p. taking into consideration the tensional forces
of the dislocations which constitute a grain boundary.
Dislocation is a structural fault in the lattice, caused
by partial slipping of atoms on the slip plane. The atoms
in close vicinity of dislocations exist under severe
strain such that within the core, elastic stress field
breaks down. Compressional and tensional forces act on
atoms lying on two sides of the slip plane as shown in
fig. 50. Knowing the stress value at the dislocation
site, depression in m.p. could be evaluated using
Clausius-Clapeyron eqn.
\[ \Delta t = \frac{T (V_L - V_s)}{L} \cdot \Delta \rho. \]  

(4.1)

where \( V_L - V_s \) is the difference in specific volumes of the metal in liquid and solid state, \( T \) the melting point in °K, and \( L \) the latent heat.

The largest normal stress at the dislocation site, according to Cottrell, (1953) is given by

\[ \sigma_{\text{ww}} = - \frac{D}{\gamma} \cdot \sin \theta. \]  

(4.2)

where \( D = \frac{\mu L}{2K(1 - \nu)^2} \).

The stress is compression above the slip plane and tension below it, and decreases as distance from dislocation increases to infinity. The strain on the atoms surrounding the dislocation can be found by averaging the stress equation up to \( \infty \). Considering that lowest dislocation density for annealed crystals is of the order of \( 10^8 /\text{cm}^2 \), the distance between dislocations would be \( 10^{-4} \text{ cm} \). The limit of \( \infty \) would therefore, be replaced by this value.
The average stress at the dislocation site is given by,

$\sigma_{yy} = \frac{\int_{0}^{\theta} \sigma_{yy} \cdot d\theta}{\int_{0}^{\theta} d\theta}$

(4.5)

Substituting $\mu = 1.9 \times 10^{11}$ dynes/cm$^2$, $\nu = 0.33$, and $b = 5.331$ Å in the equation, the average stress value comes out to be $3.406 \times 10^7$ dynes/cm$^2$ in case of tin. Using this value for $\Delta \Phi$ in eqn. (4.1) and substituting $T = 805 K$, $V_L - V_S = 0.004$ cc, and $L = 14$ cal., the depression in m.p. at dislocation site is found to be 0.1174°. This value of depression in m.p. due to purely tensile stresses is comparable to the values obtained by Chalmers.

**Grain boundary structure & preferential melting.**

This treatment could further be extended to the (van A.A., Shaw, 1955) grain boundaries. The simplest 'tilt' boundary is assumed to be one in which two crystals of simple cubic
shear stress at a point \((x,y)\) on the slip plane containing the dislocation is given by the sum of stresses due to all the dislocations in the row. It is given by,

\[
\sigma_{xy} = \frac{\mu b}{2\pi (1-\nu)} \sum_{-\infty}^{\infty} \frac{x^2 - y_n^2}{(x^2 + y_n^2)^2} 
\]

(4.4)

where \(y_n = y + n b\) , and \((\sigma_{xy} = \sigma_{yx})\).

The sum as evaluated by Burgers is given by:

\[
\sigma_{xy} = \frac{\mu b}{2\pi (1-\nu)} \frac{\kappa^2 \chi}{k^2} \frac{(\cos \lambda \frac{\kappa x}{h}) (\cos \frac{\kappa y}{h}) - 1}{2 \left( \sin \lambda \frac{\kappa x}{h} + \sin \frac{\kappa y}{h} \right)^2} .
\]

(4.5)

At large distances \(x >> h\) , the stress falls off exponentially as shown by following expression:

\[
\sigma_{xy} \sim \frac{\mu b}{2\pi (1-\nu)} \frac{\kappa^2 \chi}{k^2} \frac{\frac{\kappa x}{h}}{4 e} \cos \frac{2\kappa y}{h} .
\]

(4.6)

In order to obtain large range stress on the slip plane containing one of the dislocations, put \(y = 0\) , in the expression. The simplified value is given by

\[
\sigma_{xy} = \frac{\mu b}{2\pi (1-\nu)} \frac{\kappa^2 \chi}{k^2} \frac{1}{\sin \lambda^2 \frac{\kappa x}{h}} .
\]

(4.7)
This expression when used for calculating the strain energy per dislocation or per unit area of the boundary, is integrated along the slip plane from \( \gamma = 0 \) to \( \gamma = \infty \). \( \gamma_0 \) is the radius of a small circle enclosing the dislocation. This expression can also be used for evaluating depression in melting point along the grain boundaries. Though the stress field theoretically extends upto \( \infty \), it decreases exponentially. In calculating the average stress value the theoretical limit of \( \infty \) would be replaced by a distance of \( 10^{-4} \) cm. due to presence of other mosaic boundaries in the crystals. X-ray analysis shows that mosaic blocks are about \( 10^{-4} \) cm in dimensions. The value of \( \gamma_0 \) was determined by putting \( \Theta_m = \frac{b}{2 \pi \gamma_0} \) where \( \Theta_m \) is the angle for which boundary has maximum energy. For the value of \( \Theta_m = 12.6^\circ \) in case of tin, \( \gamma_0 = 4.266 \times 10^{-4} \) cm. The average stress values are given by equation (4.8).
Depressions of m.p. calculated by substituting average stress values in Clausius-Clapeyron eqn. (4.1) are given in Table 3.

<table>
<thead>
<tr>
<th>Boundary angle in degrees</th>
<th>Average stress in dynes/cm² x 10²</th>
<th>Depression in melting point °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>5.081</td>
<td>0.175</td>
</tr>
<tr>
<td>10</td>
<td>3.071</td>
<td>0.111</td>
</tr>
<tr>
<td>10.5</td>
<td>2.636</td>
<td>0.091</td>
</tr>
<tr>
<td>14</td>
<td>2.336</td>
<td>0.080</td>
</tr>
<tr>
<td>30</td>
<td>1.356</td>
<td>0.0121</td>
</tr>
</tbody>
</table>

It is to be seen from the table that, whereas depressions in m.p. for small-angle of misfit boundaries are in fair agreement with the observed results, the values are far too low for large-angle boundaries. The reasons for such disparity in results become apparent if stress fields of boundaries are more critically examined. Read (1963) has shown that shear stress on the slip planes...
of dislocations involved in stability equation of boundary, is an infinite series with higher terms. Whereas these terms are not significant for small values of 'e', their contribution cannot be neglected when dislocations come nearer. For large angle boundaries, the stress fields of various dislocations are superposed. As the spacing between dislocations decreases, nonelastic stresses of core would also overlap high elastic fields of dislocations and would materially influence the resulting distortion at the site. It is not possible to visualise accurately the change that would occur in the dislocation model of the boundary on this account.

**Meltine of large-angle boundaries.**

Modifications to the dislocation model so as to include large angle boundaries have been suggested by Smoluchowski (1956), Friedel et al (1953), and Lemor and Nye (1953). Smoluchowski's model seems to be of greater significance in this case. According to this theory, boundary dislocations which are separated by undistorted regions.
condense to form bigger regions of distorted lattice.
These regions are supposed to be dislocations with large Burgers vectors (Eq. 50).

The concept, however, suffers from certain drawbacks. The critical stage at which Burgers vectors for dislocations of the boundaries would increase is not clearly defined. In case the model be adopted for evaluating depression in m.p., some arbitrary values of angles of boundaries at which large dislocations are formed, will have to be accepted. The increase in Burgers vector will also be integral as it would be brought about by a further slip in the slip direction of the dislocation.

Read and Shockley (1959) have shown that for a 0.4° boundary, dislocations exist in every sixth atomic plane. Slight increase in 'θ' is sufficient to cause irregular spacing of dislocations. The boundaries having θ greater than 10° should be treated as large angle boundaries as the dislocations some very close to each other. Following Smoluchowski's model, if it is assumed that strength of dislocations for a 0° boundary is twice that of a 10°
boundary, the dislocation spacing and structure of two boundaries would be identical. Structures of boundaries with angles lying between 10° and 20° would be comparatively complicated. For convenience, it has been arbitrarily assumed that after every 10°, the Burgers vector of dislocation increases by unity. It is to be pointed out that stability of such large dislocations has not been taken into consideration here.

The depressions in m.p. were calculated by substituting multiples of Burgers' vector in stress equation (4.7), and have been given in table 4.

<table>
<thead>
<tr>
<th>boundary angle in degrees</th>
<th>Burgers' vector in cm. x 10^-3</th>
<th>Average Stress in dynes/cm² x 10^7</th>
<th>Depression in m.p. in °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>1 x 5.631</td>
<td>5.081</td>
<td>0.175</td>
</tr>
<tr>
<td>10</td>
<td>1 x 5.631</td>
<td>3.071</td>
<td>0.11</td>
</tr>
<tr>
<td>14</td>
<td>2 x 5.631</td>
<td>8.344</td>
<td>0.287</td>
</tr>
<tr>
<td>18</td>
<td>2 x 5.631</td>
<td>9.663</td>
<td>0.333</td>
</tr>
<tr>
<td>25</td>
<td>3 x 5.631</td>
<td>10.470</td>
<td>0.350</td>
</tr>
<tr>
<td>30</td>
<td>3 x 5.631</td>
<td>6.845</td>
<td>0.339</td>
</tr>
</tbody>
</table>
Fig. 51. GRAIN BOUNDARY MELTING IN ICE.
\((x \times 4/10)\)
It is interesting to note that though calculated values for depression in m.p. differ from the experimentally determined values, both are comparable. The values for boundaries from 1° onwards are nearly constant. It is also to be pointed out that since \( \theta \) and \( (90 - \theta) \) boundaries are symmetrical, the dislocation distributions for them would be identical. As such an 80 degree boundary would exhibit same depression as a 10 degree boundary.

**Fusion of crystal boundaries in ice.**

The above discussion shows that depression in m.p. at boundaries would occur even in absence of impurities. Experimental support to this was obtained in the studies of grain boundary melting in polycrystals of ice. It was found that when a specimen of commercial ice was exposed to heat radiations under suitable conditions, preferential melting on the surface occurred along boundaries giving the appearance of distorted hexagonal patterns. Fig. 51 (XI/10) shows a typical enlarged
reproduction of a photograph of ice surface. Observations of inhomogeneous melting on the surface have also been made by a number of workers. While investigating the glacier flow, Renaud (1949), from an analysis of salt content of water taken from various regions of ice crystals, concluded that the preferential melting of the boundaries was due to the presence of brine film along them. The boundaries in this case were not found to behave as amorphous ones.

However, studies of ice prepared from air-free redistilled water have shown similar melting at the boundary sites. Ice crystals from air-free distilled water were grown in a refrigerator. The specimen showed fine lines in the interior. When exposed to heat radiations, melting seemed to start in the form of etch pits at points cut by these lines. With progress of time more etch pits appeared between them and later joined up to form patterns as seen in Fig. 5. The melting was not superficial. It occurred throughout the thickness of the crystals. On application of slight pressure various crystals separated out along prismatic planes. These observations were made
visually.

These observations could in no way be correlated with the presence of impurities along the boundary sites. It is suggested that such melting would result due to preferential melting of atoms at those sites as they exist in conditions of strain. Since ice crystals are known to exhibit metallic tendencies, it is further suggested that 'transition lattice' concept can be extended to its boundaries as well.
The preferential melting of grain boundaries in polycrystalline aggregates has been discussed in terms of their dislocation structures. The atoms in close vicinity of dislocation exist under severe strain as compressional and tensional forces act on the two sides of the slip plane. These atoms would exhibit preferential melting.

Using the expression for maximum normal stress at the dislocation site, \( \sigma_n = -\frac{P}{r} \cdot \sin \theta \) (Cottrell, 1953), for finding average elastic stress values, depression in melting point was evaluated by applying Clausius-Clayperon equation. In case of tin, the depression in m.p. was found to be about 0.12°C.

The treatment was extended to grain boundaries, which are considered to be rows of dislocations. The average stress values for these boundaries were evaluated taking into consideration their stability equations. The shear stress acting on the slip plane in these cases acts normally to the boundary interface, and is given by (Cottrell, 1953).
\[ \tau_{xy} = \frac{\mu \cdot b}{2 \pi (1 - \nu)} \cdot \frac{\kappa^2 \gamma}{k^2} \cdot \frac{1}{\sinh k R / \lambda} \]

Theoretically the stress is supposed to extend from the dislocation core to infinity, but for finding average stress values an upper limit of $10^{-4}$ cm. was taken in view of the presence of other mosaic blocks. Depression in m.p. have been evaluated in case of tin for boundaries of different orientations. The values, though comparable with the experimentally determined values of Chalmers (0.14°C), were found to decrease with increasing angles of misfit. A modification of the dislocation model of the boundaries in accordance with Smoluchowski's concept was found to bring about a better agreement between the experimentally measured and calculated values.

Preferential melting of grain boundaries in polycrystalline ice prepared from redistilled water has also been recorded.
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