Section 3.

Etching of Polycrystals under Cathodic Sputtering.

Among the structure-sensitive characteristics of polycrystals, grain boundaries are important as they are regions of atomic misfit in the aggregate. Recently, these have been found to consist of rows of dislocations. Important information regarding the dislocations has been obtained from the study of surfaces on which they emerge as in case of crystal growth. Etching is another important technique used for this purpose. In the earlier work, usually, thermal and chemical etching were employed. The investigations revealed the formation of grooves in Cu, Zn and Ag during thermal etching (Chalmers, 1957), 'veining' structure of boundaries in aluminium during chemical etching (Incombe, 1948), and the appearance of etch pits on Ge (Vogel et al, 1953) and on Al (Hirsch, Horne & Whelan, 1967) at the boundary sites.

In the work reported in this section, cathodic sputtering in argon was employed as the etching technique.
The investigations were undertaken chiefly to assess the suitability of the phenomenon for revealing dislocations and other structure sensitive characteristics of polycrystals. Earlier, it was employed by Necutcheon and Pahl (1940) for the etching of steel alloys and by Fisher and Webbar (1950) for microdiffusion studies in metals. Recently, etch effects on metal surfaces caused by low and high energy ionic bombardment have been studied by some other workers as well (vide infra).

Cathodic sputtering is a gaseous discharge phenomenon and its various theoretical aspects have been developed by Gunthershulze and Blonschmidt, Glocker and Lind (1939), Seeiger (1940), Towns (1944), Nasrey and Burnhop (1950) and others. During sputtering the cathode is constantly bombarded by high energy ions. These ions impart their energy to the metal atoms and cause spontaneous evaporation over areas of atomic dimensions. Towns (1944) estimated that very high temperatures exist over a small region of the cathode surface for a small fraction of time of the order of $10^{-6}$ seconds. He further showed that the extent
Fig. 25
of sputtering was largely dependent upon the ion-current density, voltage across the anode-cathode gap, the pressure inside the chamber, and upon the physical dimensions of the unit. According to Wenner (1937), the energy is transmitted by 'momentum transfer' process, and the removal of metal occurs due to the impact of high energy ions. Megutcheon and Pahl (1949) also observed that the removal of metal from the surface is subject to the application of a minimum potential below which sputtering does not occur.

Experimental.†

In these investigations, slow sputtering was carried out to reveal the structural characteristics of the crystals and at the same time to allow the specimen to retain sufficient polish for interferometric examination. A simple sputtering unit as shown in Fig. 25 was set up. It consisted of a strong bell jar (diameter 8" and height 10") which was used as the discharge chamber. The neck of the jar was sealed vacuum tight by a stopper through

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which an aluminium rod was passed. The metal specimen to be etched formed the cathode and was fixed to the rod with the help of a screw thread. The anode consisted of an aluminium disc of diameter 4" attached to a brass box by an adjustable screw; the box in turn being attached to an earthed brass base plate. Aluminium electrodes were used because of their low sputtering rate. The jar was sealed to the base plate by smearing a low vapour pressure vacuum wax around its base; all other joints being sealed and made vacuum tight by sealing wax. The base plate was provided with openings which connected the discharge chamber to an Edward's two stage by pass pump and to the gas supply. The sealings were made perfect to maintain very low pressures of the order of a mm. of Hg. in the discharge chamber.

The potential to the cathode was applied from a 50 cycle A.C. transformer. It was rectified by an RCA 866A/866 half wave rectifier and was controlled by a variac in the primary. Filament voltage to the rectifier was fed from an oil immersion step down transformer also controlled by a
varied in the primary. Usually, low voltages in the range of 300 to 500 volts were applied in order to reduce the ionic energy. This was done to avoid severe etching of the specimen. During experiments flushing atmosphere of argon was maintained in the discharge chamber. The cathode-anode gap was kept 0.2 to 3 cm, and the gas pressure of the order of a mm. of Hg. was so adjusted that cathode dark space was nearly touching the anode. An increased size of dark space besides representing the reduced pressure in the discharge chamber, also increases the mean free path ($\lambda$) for the gas ions. $\lambda$ is known to be only a fraction of dark space. With large value of free path of the ions, the probability of back diffusion of sputtered atoms to the cathode is also reduced.

A number of bronze and babbit alloys of different compositions, and polycrystalline tin were etched under cathodic sputtering. The specimens were mechanically polished before sputtering. The etched specimens were later examined by high resolution microscopy and multiple beam interferometry. The results have been divided in two parts; part A
deals with the sputtering characteristics of alloys and part B with the differential sputtering of grain boundaries of polycrystalline tin.

Results and Discussions.


Cold-worked specimens of Sn-Cu bronze (composition 9% Sn, 91% Cu, and 80% Sn, 20% Cu), Al-Cu bronze (30% Al, 70% Cu), Sn-Sb babbitt (7% Sb, 93% Sn) were sputtered under conditions described earlier. The investigations revealed interesting information regarding the sputtering characteristics of growth and precipitate patterns of alloys and grain boundaries of polycrystals. The interferometric examination exhibited the changes occurring at the grain boundaries during sputtering.

Graining Structure in Cu-Sn Alloy.

Sn-Cu bronze specimen subjected to sputtering belonged to binary alloy system with an excess of either copper or
Fig. 26. SHOWING DENDRITES IN BRONZE AFTER 8 HOURS OF SPUTTERING. X 55

Fig. 27. SAME AS Fig. 26. AFTER 12 HOURS. X 55
Fig. 28. 'Veining Structure in Bronze. x55
tin in the matrix. These metals exhibit considerable influence on the etching characteristics of the alloys. Fig. 26 (X 55) and Fig. 27 (X 55) are two typical micrographs showing the sputtered surface of the alloy rich in copper. The etching was carried out for 8 and 10 hours respectively at a potential of 300 volts. The severely etched surface reveals the segregation of dendrite phase in the matrix. The grains of the specimen are rendered visible by the differential orientation of the tree-like dendrites. Fig. 28 (X 55) shows the sputtered surface of the other specimen rich in tin after 10 hours of sputtering at 300 volts. Dendritic precipitation of Cu-Sn phase is not seen in this case. A closer examination of the sputtered surface reveals a 'veining' structure within the etched zones of the matrix.

In binary alloy systems usually, the composing metals combine to form two homogeneous coexisting phases. The association and distribution of the phases give the alloys their distinct structure, e.g., eutectic, peritectic, dendrite and others. In alloys where two phases crystallise from melt, dendrites are quite common. They characterise
the nonequilibrium conditions during growth. Equilibrium diagrams of Cu-Sn system exhibit limited region of homogeneous solubility for the components. Homogeneous alpha phase exists up to 18% tin, with larger percentage of tin harder component of Cu₃Sn crystallises.

The preferential sputtering of dendrites in the copper rich alloy shows that they are signs of weakness in the alloy system. They exhibit comparatively low corrosion resistivity when subjected to ionic bombardment. Copper has a higher sputtering rate in argon as compared to tin. Low corrosion resistivity of Cu rich alloy during sputtering can, therefore, be attributed to this fact as well. The veining structure revealed in case of tin rich alloy confirms such a conclusion. 'Veining' occurs due to the removal of Cu atoms from these sites. Thus cathodic sputtering is similar to the preferential etching action of a chemical etchant. Evidence for this also came from the examination of anode of the sputtering unit which was found to be covered with a thin brown layer of Cu atoms.
Fig. 29. PREFERENTIAL SPUTTERING OF GRAIN-BOUNDARIES IN AL-CU. BRONZE. X55
Dislocation etch pits along boundaries in Al-Cu alloy.

The Al-Cu alloy specimen subjected to sputtering in these investigations also contained an excess of copper. In Al-Cu system, though a number of phases exist, the solubility of Cu in aluminium is fairly low. An eutectic is known to form at 33% copper content. Addition of copper is also known to decrease the corrosion resistance of aluminium. The results were found to be of special interest so far as the etching of grain boundaries were concerned.

Fig. 29 (X 55) is a typical micrograph of the surface after 15 hours of sputtering at 400 volts. The etching has revealed randomly distributed precipitates in the matrix. Whereas the general matrix undergoes mild etching, the precipitates remain unspattered due to their higher hardness value. A closer examination (enlargement) of the micrograph (fig. 29) shows that etching has exposed the granular structure of the alloy. The average grain size is of the order of about $10^{-3}$ cm. The micrograph also shows
Fig. 30 . X 55

Fig. 31 . X 450

DELINEATION OF BOUNDARIES (Al-Cu) INTO ETCH PITS.
preferential sputtering of the grain boundaries which appear as deeply etched lines. At a number of places these lines have been resolved into rows of etch pits (fig. 30). The etch pits, however, do not exhibit any regular spacing.

Increase of sputtering time only led to severe etching of the specimen without furnishing any additional information. Fig. 31 (X 450) is a micrograph of the surface, after the alloy had been subjected to 50 hours of sputtering in shifts. The surface appears severely etched, and covered with circular etch pits. The boundaries are, however, easily distinguished as rows of etch pits.

Grain boundary etching in Sn-Sb babbitt alloy.

The etching of Sn-Sb babbitt alloy also yielded some interesting information regarding the grain boundaries of the alloy. The specimen subjected to sputtering had a large grain size, and a random distribution of Sn-Sb superlattices. Since the sputtering rates of antimony and tin in argon are comparable, to increase the probability
Fig. 32. Preferentially sputtered boundaries in Sn-Sb babbit. X 100

Fig. 33. Sputtered boundaries (dark illumination) X 50
of differential etching of components low energy ions were employed and sputtering potential was maintained at 300 volts.

It was found that whereas grain boundaries appeared even after a small sputtering time, they became more distinct only after prolonged etching. Fig. 32 (X 100) is a typical micrograph of the surface subjected to 15 hours of sputtering, showing severe preferential etching of \( \text{polyester-1} \) along the grain boundaries. Sputtering has also occurred along the rectangular and triangular facets of areas of the order of \( 10^{-3} \) sq. mm. These facets are the Sn-Sb superlattice in the matrix. Whereas the micrograph shows mild etching of the specimen in general, certain areas other than boundaries are also characterised by severe attack.

Micrograph 33 (X 55) shows the effect of long time sputtering at low voltages. The micrograph taken under dark illumination shows the etched boundaries as white lines. It is further revealed that at low voltages even long time sputtering is not sufficient for the etching of superlattice.
It has already been mentioned that grain boundaries do not have a normal structure. Preferential sputtering of grain and subgrain boundaries in babbit and Al-Cu alloy is therefore, directly related to their structure. According to 'transition lattice' theory, the boundary is considered to be an array of dislocations. The atoms at the site of dislocations exist in a state of strain, and as such are apt to be sputtered. Evidence of such etching is present in the work of Vogel et al (1958) on germanium, and Hirsch, Horne and Whelan (1957) in case of aluminium (vide supra).

It was found in these investigations that, whereas the grain boundaries of babbit appeared as deeply etched lines, those of Al-Cu alloy could be resolved into rows of etch pits. In accordance with theory, the etch pits would correspond to the dislocation sites along the boundaries. The delineation of etch pits was, however, confined to only those areas where the orientation difference between adjoining grains was small. It is possible to evaluate the orientation differences between the grains
from etch pit spacing provided it is uniform. Regular distribution of etch pits was not noticed.

Recently Wehrar (1958) has also reported similar results of etching under ionic bombardment in case of germanium and other crystals. The grain boundaries appeared as deeply etched furrows. Jolsky (1958) and Konig (1958) have observed etch pits at dislocation sites in the single crystals of Ge and Si. During these studies differential sputtering of tri-crystal boundaries of polycrystalline tin was also recorded and has been discussed at a later stage.

The corrosive properties of boundaries in metals and alloys also depend upon the presence of impurities at these sites. The impurities may be in the form of foreign atoms of solids or adsorbed gases. Diffusion of foreign atoms to the dislocation sites and boundaries is an interesting phenomenon. Dean, Davy and others chemically analysed the impurity content along the boundaries. Cottrell (1953) explained the sharp yield point of iron and other metals on the basis of segregated atmospheres of foreign atoms at the dislocation sites.
Fig. 34. Antimony Deposition Along Boundaries in Rabbit (Chemical Etching), x 100
Since antimony had low percentage in the babbitt specimen, its atoms diffuse to the boundaries. Evidence regarding this was obtained in the experiments (Deo & Shama, 1977) of chemical etching. Fig. 34 (X 100) shows a typical micrograph of babbitt surface chemically etched with 3% FeCl₃ solution for one minute. Though ferric chloride is known for its preferential etching action on tin, prolonged etching was found to destroy the desired result. Antimony atoms deposited along the boundaries appear as white lines. Achtar and Smoluchowski (1949) observed similar lines showing the preferential diffusion of radioactive silver along the boundaries of copper.

The sputtering rate of antimony is comparatively higher than that of tin in argon. Since differential sputtering of alloy components has also been found to occur (vide supra), it is suggested that deposition of antimony at the boundaries is an additional factor in their preferential etching. The high corrosion resistivity of Sb-Sn superlattices is, however, attributed to their higher hardness values.
Differential sputtering of grains in polycrystals.

It has been revealed in these studies that extent of etching of metals and alloys under sputtering is dependent upon their hardness values and the presence of strained material in the matrix. Whereas regions showing strains, e.g., grain boundaries are readily sputtered out, harder phases and other components remain unetched. Polycrystalline aggregates consist of grains with different orientations. Deformation of the specimen during cold-working introduces inhomogeneous microstresses in the grains. These have been extensively investigated by Smith and Stacky (1943), Lipson et al (1953), Hall (1949) and others using x-ray techniques. Hardness is also orientation sensitive property and as such varies for grains of cold-worked specimen. Polycrystals when subjected to slow and uniform etching should therefore, reveal differential etching of the grains. The sputtered specimens were examined using multiple beam interferometry. This technique is capable of providing very high depth resolution for surfaces.
Fig. 35. Polished Al-Cu Alloy (Interferogram) X 55

Fig. 36. Sputtered Al-Cu Surface (Interferogram) X 55
The metal and alloy specimens, before being sputtered, were mechanically polished on high grade emery papers, and finally on polishing machine to give good contrast to the interference patterns. Fig. 35 (X 55) is an interferogram taken on polished Al-Cu alloy surface. The wide and sharp fringes are characteristic of good polish and the flatness of the specimen. The decorative pattern revealed here is due to the presence of precipitated phase of the alloy. The mechanical polishing causes micro-abrasions on the soft phases. These are shown by fringe contours in the interferogram. Fig. 36 (X 55) shows another interferogram of the same region after the specimen had been sputtered for 9 hours at 400 volts. The specimen has undergone mild etching as shown by good contrast of fringes even after sputtering. A comparative study of two interferograms, however, shows that fringe continuity remains unaltered. No breaks or shifts are to be seen in the fringe continuity.

More interesting results were obtained in case of babbitt alloy in a series of interferograms taken on the sputtered surface. The sharp and widely spaced fringes of
Fig. 37. Fringes on Polished Babbit Alloy. X100.

Fig. 38. Appearance of shifts at boundaries after 6 hours' sputtering. X100.
Fig. 37 (X 100) are representative of the good polish and flatness of babbit. Figs. 38 to 40 (X 100) show the fringe contours on the specimen after a sputtering of 6, 15 and 40 hours respectively. A number of discontinuities in the fringes are found to appear on the sputtered surface (fig. 38). With the continuation of etching for longer intervals these fringe shifts increase in magnitude and number (fig. 39) and become widespread after prolonged sputtering (fig. 40). It is noticed that the fringe width which is dependent upon the flatness of the surface goes on decreasing from fig. 38 to 40. Various grains and boundaries of the polycrystal appear in the interferogram. They are also rendered visible by the shifts in the continuity of the fringes running across the grains. This is a marked feature. The shifts varied from a quarter to half fringe width corresponding to a level difference of e.1765 to 7730 A depending upon the time of sputtering.

Similar interesting fringe contours recorded on the superlattices are shown in fig. 41 (X 100). A fringe approaching the superlattice is found to move away in its
vicinity. The shift is due to level differences between the etched matrix and the superlattices.

In the sputtering process the specimen besides being etched, are also exposed to high temperatures for considerable time. The grains therefore, are subjected to differential thermal expansion. Carpenter and Elam (1950) have referred to the formation of grooves at the boundary sites during thermal etching. The high temperature to which the specimen are subjected during cathodic sputtering would also cause depressions at the boundaries. The fringe contours over the boundaries depend upon the nature of the groove. They would exhibit mere dip at the boundary in case the groove angle is symmetrical. In case of asymmetry, fringe shifts would be recorded (Boo & Shanker, 1958).

Though differential sputtering of grains in polycrystals is strongly suspected on the grounds of cold-working, it could not be established with certainty for the above reasons. Interference patterns on cast babbit specimen were also examined. The babbit specimen was melted and cast against optically flat glass plates kept on an
Fig. 45  X 100

Differential Sputtering of Grain Boundaries.
Part II: Differential sputtering of tricrystal boundaries in polycrystalline tin.

Specimens of high purity, well-annealed polycrystalline tin were sputtered in an atmosphere of argon under the usual conditions (vide supra). Specimens were mechanically polished before sputtering; one of them was prepared by casting tin on a flat glass plate. The dihedral angles opposite the crystal boundaries were measured microscopically. On account of etching the boundaries were not sharp and the dihedral angles could not be measured beyond an accuracy of 1°.

Typical photomicrographs of the specimens shown in Figs. 43 to 46 (X 100) indicate differential sputtering of the tricrystal boundaries in different specimens. The extent of etching of the boundary observed and the values of the opposite dihedral angles for various tricrystal sets measured are given in table 1. Investigations on thermal etching of polycrystalline metals have shown that the rate of loss of metal is always greater for those having fine grains. This has been attributed to the excess surface
Fig. 47. BOUNDARY TENSION VS. $\alpha$
free energy of the grain boundaries. On the basis of
the dislocation model of the small angle-of-misfit
boundary, this energy per unit area, according to Read
and Shockley (1949) is given by

$$E = E_0 \theta \left( A - \ln \theta \right) \quad (3.1)$$

where $\theta$ is the relative orientation difference for the
grains and $E_0$ and $A$ are constants. The number ($n$) of
dislocations per unit length of a simple tilt boundary
is given by $n = \frac{\theta m}{b}$, where $b$ is the Burgers vector.

Aust and Chalmers (1956) showed that it is possible
to compare the free energy values per unit area of
different boundaries by measuring the equilibrium dihedral
angles for the three boundaries meeting at a point. The
dihedral angles $\langle 1 \rangle$, $\langle 2 \rangle$, and $\langle 3 \rangle$ and the energy values $E_1$, $E_2$
and $E_3$ are related by the expression

$$\frac{E_1}{\sin \theta_1} = \frac{E_2}{\sin \theta_2} = \frac{E_3}{\sin \theta_3} \quad (3.1)$$
In table 1 p. 103 are also recorded the calculated values of the relative energy, the orientation difference, and the dislocation density per centimetre for the various tricrystal boundaries. The relative energy values are evaluated from the dihedral angles using equation (3.2). The energy, \( E \), of the most etched boundary is taken as the unknown unit of energy in each case. The values of \( \theta \) corresponding to boundary energies are obtained from Fig. 43 which is plotted on the basis of Aust and Salmer data for energy variation with \( \theta \) to fit equation (3.1).

From the knowledge of \( \theta \), the number of dislocations per centimetre along the boundaries (assumed to be of the simple tilt type) are evaluated, using Burgers vector \( b = 5.43 \) Å.

It is seen from the data presented in table 1 that the relative energy values are in order of decreasing magnitude from the most to the least etched boundary in the first two cases. The same is true of the dislocation densities. In the other two sets, however, the relative energies of the tricrystal boundaries are comparable, but the extent to which they are etched is different. This
<table>
<thead>
<tr>
<th>No.</th>
<th>Grain Boundary</th>
<th>Opposite dihedral angles (°)</th>
<th>Relative boundary energies (E)</th>
<th>Relative difference in orientation (°)</th>
<th>Relative dislocation density X 10^6</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Most etched</td>
<td>101</td>
<td>1.000</td>
<td>9</td>
<td>2.685</td>
</tr>
<tr>
<td></td>
<td>Moderately etched</td>
<td>119</td>
<td>0.839</td>
<td>7.01</td>
<td>2.200</td>
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<tr>
<td></td>
<td>Least etched</td>
<td>141</td>
<td>0.641</td>
<td>3.6</td>
<td>0.93</td>
</tr>
<tr>
<td>2</td>
<td>Most etched</td>
<td>110</td>
<td>1.000</td>
<td>9</td>
<td>2.685</td>
</tr>
<tr>
<td></td>
<td>Moderately etched</td>
<td>120</td>
<td>0.900</td>
<td>7.10</td>
<td>2.155</td>
</tr>
<tr>
<td></td>
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<td>1°8</td>
<td>0.839</td>
<td>6.10</td>
<td>1.856</td>
</tr>
<tr>
<td>3</td>
<td>Most etched</td>
<td>119</td>
<td>1.000</td>
<td>14.36</td>
<td>4.399</td>
</tr>
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<td>1.016</td>
<td>14.24</td>
<td>4.309</td>
</tr>
<tr>
<td></td>
<td>Least etched</td>
<td>1°6</td>
<td>0.916</td>
<td>7.24</td>
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<td>4</td>
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<td>Moderately etched</td>
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<td>4.197</td>
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<td></td>
<td>Least etched</td>
<td>1°0</td>
<td>0.979</td>
<td>8.30</td>
<td>2.545</td>
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Fig. 48. Graph for rel. energy vs. $\theta$, for grain boundaries of tin (Aust & Chalmers' data).
anomaly can be explained if the etching is correlated with dislocation densities choosing higher values of corresponding to energies of the most and the moderately etched boundaries.

For any value of energy near the maximum, $\theta$ has two values. The values of $\theta$ when $E_1 = 1$ are recorded in Fig. 43. The same holds good for the dislocation densities which depend upon $\theta$. For higher values of $\theta$, chosen against the energies of the most and the moderately etched boundaries (Table 1, sets 3 and 4), the corresponding dislocation densities are in order of decreasing magnitude from the most to the least etched boundary, though the energy values do not follow the same order (Table 1). Evidence is available from the work of Loew and Yarnai (1947) on the chemical etching of aluminium that intercrystalline attack at the boundaries depends upon the orientation of the adjoining grains. Considerable evidence for the etch pits at dislocation sites has also been obtained (vide supra). The above result, that the etching of the boundaries under cathodic sputtering can be better correlated with their dislocation densities than with their energy values,
would appear to be significant for the transition lattice theory of the grain boundary (Deo & Sharma, 1958)


e N E M A B Y

Metal and alloy crystals have been etched under cathodic sputtering to assess the suitability of the technique for revealing dislocations. A cathodic sputtering unit was set up for etching the crystals at low applied potentials. Polycrystalline specimens of Al-Cu and Cu-Sn bronze, Sn-Sn babbitt and pure tin were sputtered in flushing atmosphere of argon for different durations. The etched crystals were examined using high resolution microscopy and multiple beam interferometry.

The investigations revealed that etching of alloy crystals depends upon the sputtering rate of the composing metals in argon, hardness of various phases precipitated in the matrix and the presence of grain boundaries. For example, the etching of Sn-Cu bronze specimen showed preferential sputtering of Cu-rich dendrites, and removal of Cu-atoms from the harder phases of the alloy. The latter caused the appearance of a 'veining' structure on the etched surface.
Low corrosion resistance of Cu-rich dendrites and 'veining' structure are due to high sputtering rate of Cu in argon. Both Al-Cu bronze and Sn-Sb babbitt specimens exhibited preferential etching of the grain boundaries. The grain boundaries are known to be regions of atomic misfit between the grains, and according to 'transition lattice' concept, these are rows of dislocations. Atoms at the dislocation site being under a state of strain are apt to be etched (sputtered) preferentially. The dislocation structure of boundaries was revealed in the etching of Al-Cu bronze. At a number of places the etched boundaries were resolved into rows of etch pits. Superlattices, however, remain unetched due to their hardness values. Boundaries also act as sinks of impurity atoms in the matrix, as these diffuse to dislocation sites. Chemical etching of babbitt with acidulated FeCl₃ solution showed the deposition of antimony atoms along the boundaries.

The interferometric examination of etched crystals revealed some other interesting characteristics of the boundaries. It was found that interference fringes recorded
shifts as they passed over various grains of the etched specimen. Since the specimens were cold-worked before being etched, the grains were expected to exhibit differential etching. The fringes in such cases would show sharp breaks as they cross the boundaries. Differential etching, however, could not be established with certainty as similar results are obtained when specimens are annealed. As the grains try to assume equilibrium shapes, boundary tensions become operative and cause level changes at the boundary sites. Interference fringes, as they pass, show sharp breaks of varying magnitudes.

The etching of polycrystalline tin also revealed another interesting feature, i.e., differential sputtering of tricrystal boundaries. It was found that this could be correlated with the dislocation structure of the boundaries. The relative grain boundary energies were evaluated from the measured dihedral angles, taking the energy of the most etched boundary as the unknown unit of energy. The orientation difference (θ) between grains for various tricrystal boundaries were obtained from Aust & Chalmers' data for the boundary energy variation with (θ) in case of tin. The
dislocation densities for the boundaries were calculated for various values of \( \Theta \). It was found that differential etching of boundaries could be better correlated with the dislocation densities.
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Fig. 49. Preferential Melting of Boundaries in Tin, x55.