AUTHOR

R. N. KING.

TITLE

THE MECHANICAL PROPERTIES OF CERTAIN TIN BASED ALLOYS

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"The Mechanical Properties of Certain Tin Based Alloys"

by

Roger King

A Thesis submitted to The University of Surrey for the Degree of Doctor of Philosophy.

October 1980
Abstract

The changes that accompany the plastic deformation of pewter have been studied by microscopical, thermal and analytical techniques in addition to the measurement of mechanical properties.

It has been found that deformation facilitates the decomposition of the supersaturated tin based solid solution formed on casting, with the consequent precipitation of the β phase (SbSn). Recrystallisation occurs in pewter alloys at room temperature, and the fine recrystallised grain size is stabilised by the fine dispersion of SbSn.

At room temperature and above it is shown that rolled pewter with a sufficiently small grain size can deform at least in part by a superplastic mechanism, which involves grain boundary sliding, at a lower stress than would otherwise be necessary for slip on a macroscopic scale.

The softening of rolled pewter as measured in a conventional hardness test is found to be a direct consequence of the increased creep rate due to grain boundary sliding during the indentation period. This has been confirmed by tensile testing at low strain rates where rolled pewter is shown to have a lower strength than cast pewter of the same composition.

At high rates of testing this loss of strength
is not shown as the grain boundary sliding mechanism is unable to make any significant contribution to deformation.

Alternative alloy compositions have been developed that do not show such severe softening as conventional pewters at large rolling reductions.
I would like firstly to thank my supervisor Dr. B.L. Daniell for his advice, encouragement and many helpful suggestions in the preparation of this thesis and the preceding practical investigation.

I would also like to thank the staff and technical staff of the Dept. of Metallurgy and Materials Technology for useful discussions and practical assistance, and Prof. M.B. Waldron for making laboratory facilities available to me.

I am also very grateful to the staff of Fry's Metals Ltd for undertaking chemical analysis, the production and supply of alloys and materials, and for typing this thesis in addition to many helpful discussions. Thanks are also due to the Tin Research Institute for interesting discussions and the use of library facilities.

Further acknowledgements are made to Fry's Metals Ltd and the Worshipful Company of Pewterers for financial support without which this investigation would not have been possible.
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List of Symbols and Abbreviations

A  - a constant.
a  - Time in secs. to reach load in a hardness test.
B.H.N. - Brinell Hardness Number.
c  - Atomic concentration of solute.
D  - Diameter of Brinell hardness indentor.
d  - diameter of indentation.
Fv  - Volume fraction.
L  - Load in a Brinell hardness test (kg).
L.S.F. - Linear size factor.
m  - Strain rate sensitivity factor.
n  - Stress exponent.
Q  - Activation energy.
R  - Gas constant.
r°  - Seitz radius of an atom.
rp  - Mean particle radius.
T  - Absolute temperature (°K).
Tm  - Melting temperature (°K).
t  - Indentation time.
V.P.N. - Vickers Pyramidal Number.

δ  - Missfit parameter of a solute atom.
ε  - Strain.
\dot{\varepsilon}  - Strain rate.
μ  - Shear modulus.
μm  - micro meter.
σ  - Stress.
\( \sigma_y \) - Yield stress.

\( n \) - Atomic volume of an atom.
Tin, suitably hardened, has a long history of use for domestic and artistic objects. Until recent times the usual hardener for tin was lead, but the alloy so produced has the disadvantage that it rapidly loses its brilliant lustre and goes grey or black. In addition it is very susceptible to corrosion and can present a health hazard. Modern pewter is virtually lead free (0.5% max)(1), and contains antimony and often copper as the hardening additions.

It is not known when antimony was introduced as an alloying constituent in tin, but its regular use seems to date from the invention of Britannia Metal in the middle of the 18th Century. In this alloy the antimony ranged from 2-5% according to the hardness desired. Antimony does not seriously affect the colour of tin, nor does it encourage tarnishing. Its hardening action is fully compatible with that of copper, and both additions are used in their appropriate amounts.

An antimony content of 4% used to be preferred for pewter intended for spinning, while a casting alloy of up to 8% antimony and 2% copper had a higher hardness, but was more difficult to work. At the present time the most popular composition is an alloy containing 6% antimony and 1½% copper. This is adequately hard in the cast conditions and yet still soft enough to
Pewter today does not enjoy the same popularity as in the past, and many of its applications have been taken over by stainless steel. Commercially however it still has some importance, and over 1000 tons of ingots and rolled sheet are produced in the UK each year at a value of approximately £8 million.

Perhaps the major disadvantages of pewter compared with its competitors are its low hardness in the cast condition (20-25HV) and the unusual softening that takes place on rolling that can reduce the hardness even further. This is a considerable problem, particularly at the present time when many of the intricate thin castings of the past are now being replaced by pressings made from rolled sheet. The softening is of great detriment to the material, since although it is easily worked, thicker sections must be used in many applications to give adequate strength and creep resistance and the surface has a tendency to "scuff" and is easily scratched. Rolled pewter can be easily recognised, as when struck it gives a dull thud similar to lead, whilst cast pewter gives a metallic ring.

Much of the lost hardness due to rolling, and the metallic ring, can be restored by a simple heat treatment at temperatures between 150°C and 220°C. Unfortunately there is great resistance by most
Pewterers towards heat treatment since this is a craft industry rather than a technologically based one. There is also a reluctance to invest in the necessary equipment which would add another stage to the manufacturing process, and in addition there are problems involved in heat treating finished articles due to the low melting point solders used in their construction. Clearly a pewter which does not soften appreciably on working, and preferably has a higher hardness than conventional alloys would be of great commercial advantage to a manufacturer selling rolled sheet to craftsmen.

What is required is a commercial as well as a technological solution to the problem of hardening tin. This puts several constraints on any solution. Alloying additions must be nontoxic and relatively cheap. In addition a similar colour to existing pewters is required along with good casting properties, extensive ductility and low earing properties.

This research is directed towards an understanding of the processes involved in the 'work softening' and subsequent hardening of rolled pewter sheet, in the hope that an improved alloy may be developed.
2. Properties of Tin and Pewter

Tin in the form in which it is generally familiar is a soft white lustrous metal of low melting point. Another allotropetic form known as grey tin is stable below 13.2°C. The transformation from the familiar white tin to grey tin is exceptionally slow at normally encountered temperatures, and may take several hundred years. All references to tin in this report may be understood to refer to white tin. Many of the physical constants and mechanical properties of tin have been collected by the Tin Research Institute. The lattice structure of tin has been determined by Lee and Raynor, and was found to be body centred tetragonal of the A5 type (a = 5.8199 kx, c = 3.749kx, C/a = 0.5455 at 25°C).

Investigations on the deformation of single crystals of tin under tension have shown that glide may occur on one of several planes, that which is effective being the one on which the critical shear stress is first reached. Table I gives data on the slip of white tin with an impurity content of 0.0001% (4). The critical shear stresses given in the table are the stresses at which appreciable deformation occurs in comparatively short time tests. It has been shown by Chalmers (5, 6) that a slight plastic deformation occurs by creep in single crystals at stresses as low as 0.1 MPa. (\( \dot{\varepsilon} = 3 \times 10^{-8}/\text{min} \)). When larger stresses are
applied the initial creep rate is proportional to the stress for stresses up to a fairly definite value, after which the creep rate increase much more rapidly with stress.

This rapid increase in creep rate corresponds to the yield stress as detected by less sensitive methods, and when resolved along the slip planes in the slip directions is of the same order as the critical shear stresses shown in Table I.

<table>
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<tr>
<th>Slip Plane</th>
<th>Direction</th>
<th>Crit. stress (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(100)</td>
<td>[001]</td>
<td>1.9</td>
</tr>
<tr>
<td>(110)</td>
<td>[001]</td>
<td>1.3</td>
</tr>
<tr>
<td>(101)</td>
<td>[101]</td>
<td>1.6</td>
</tr>
<tr>
<td>(121)</td>
<td>[101]</td>
<td>1.7</td>
</tr>
</tbody>
</table>

Table I

In addition to glide or slip, crystals of tin can be deformed by twinning. This takes place on planes of the (301) type when an impulsive force is applied along a direction normal to the [001] axis of the specimen. It is the process of mechanical twinning which gives rise to the "cry of tin" when it is deformed.

To bridge the gap between single crystals and polycrystalline aggregates, Chalmers studied the plastic
deformation of bicrystals at low stress\(^{(7)}\). The samples were prepared so that the crystal boundary ran down the length of the specimen. The orientation of the two crystals in the specimen was varied, and the effect of relative orientation on the yield point under tension investigated. It was found that no "micro-creep", such as was found for single crystals, occurred with these specimens, and that the tension required to cause creep at a definite rate depends on the relative orientations in an approximately linear manner, varying between 4 and 6 MPa as the angle between the c-axes of the bicrystals changed from 0 to 90°. The strengthening effect of crystal boundaries, in large grained specimens at least, was thus clearly demonstrated.

2.1 Constitution

2.1.1 The Binary System Tin-Antimony

The tin-antimony system has been studied by many investigators, who are in general agreement that the liquidus consists of three branches corresponding to the separation of three solid solutions, although their results differ in detail. The earliest diagrams, mainly determined at the end of the last century include those by Reinders\(^{(8)}\), Stead\(^{(9)}\), Gallagher\(^{(10)}\), Williams\(^{(11)}\), Puschin\(^{(12)}\), Konstantinow and Smirnow\(^{(13)}\), Guertler\(^{(14)}\) and Broniewski and Sliwowski\(^{(15)}\).
The general form of the diagram accepted today is due to Iwase et al.\textsuperscript{(16)}, and is shown in Figure 1. High purity tin and antimony were used, and the diagram was determined using differential thermal analysis, resistivity and microscopy.
2.1.1.1 The Alpha Phase Field

In the investigation by Iwase et al. (16) microscopic examination of alloys at room temperature revealed a maximum solid solubility of 8% Sb. This result was supported by the x-ray investigation of the system by Bowden and Morris-Jones (17), who found that the lattice parameter of the tin-rich solid solution increased continuously from 5.82 Å to 5.835 Å at 9% Sb and then remained constant.
An annealing treatment was used of 200 hours at a
temperature near the melting point followed by cooling
to room temperature over a period of 4 - 6 hours.

Schwarz and Summa\(^{18}\) made a complementary x-ray
investigation in 1933 which was in substantial agree­
ment with the work of the previous authors, whilst
another x-ray study along similar lines was made by
Hägg and Hybinette\(^{19}\) in 1935. A limit of solid
solubility of 9% Sb was determined at 200°C.

Hanson and Pell-Walpole\(^{20}\) confined their
attention to alloys containing up to 14% Sb. Micros­
copy showed that chill cast alloys containing up to
4% Sb consisted entirely of the primary tin rich
phase showing coring. Alloys with 4 - 10% Sb contain
in addition increasing amounts of a fine precipitate
which appeared white on etching \((\text{SbSn})\). With 10% or
more antimony the primary separation was \(\beta\) the cuboid
form of \(\text{SbSn}\), surrounded by cored \(\alpha\) with traces of
the fine \(\text{SbSn}\) precipitate.

Annealing at 190°C caused the coring to disappear
completely after approximately 14 days, but the \(\text{SbSn}\)
precipitate increased in quantity in all alloys
containing more than 4% Sb. Metallographic examination
revealed that the solubility of antimony in tin decreased
from 10.5% at 246°C to 9% at 235°C, 4% at 190°C and 3.5%
at 100°C.
These results were confirmed by resistivity measurements.

The latest and most reliable determination of the tin-rich portion of the diagram was by Eyre in 1959, who studied the $\alpha/(\alpha + \beta)$ boundary by metallography. Ingots were rolled by 50%, and then annealed at temperatures between 50°C and 223°C for periods up to 7 weeks. The following limits of solid solubility were found.

<table>
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<tr>
<th>Temperature</th>
<th>Sb Solubility</th>
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<td>50°C</td>
<td>0.75 wt %</td>
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<tr>
<td>100°C</td>
<td>1.3</td>
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<tr>
<td>150°C</td>
<td>2.2</td>
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<tr>
<td>200°C</td>
<td>4.0</td>
</tr>
<tr>
<td>223°C</td>
<td>6.6</td>
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Table 2 - Limits of Solid Solubility

These values are lower than those determined by Hanson and Pell-Walpole, and it must be presumed that the latter are in error due to insufficient annealing and their alloys were not at equilibrium. Unfortunately no annealing times are given except for 190°C. At this temperature there is good agreement between the authors. By chill casting up to 4% Sb could be retained in solid solution at room temperature.
However with supersaturated alloys spontaneous precipitation took place a few hours after quenching; so specimen preparation and examination had to be rapid. Cuboids were only observed in alloys containing more than 10% Sb.

2.1.1.2 The Beta Phase (SbSn)

Although earlier authors discussed the possibility of a number of intermetallic phases, it was found by Iwase et al.\(^{(16)}\) that all the techniques employed indicated only one, the \(\beta'\) phase with a simple cubic structure. In the same year Bowden and Morris-Jones\(^{(17)}\) published the results of a similar study using x-ray diffraction on annealed alloys. They confirmed that the intermetallic compound was SbSn, but concluded that it had an NaCl structure over the whole range of composition 41 - 54 wt% Sb. Schwarz and Summa\(^{(18)}\) were also in agreement that the SbSn phase had an NaCl structure, but considered that it had a fixed composition of 51% antimony.

Hägg and Hybinette\(^{(19)}\) made an intensive investigation of the \(\beta'\) phase field, and the authors disagreed with the findings of previous studies concerning the lattice structure. Several of the lattice diffraction lines were doubled, and from this it was demonstrated that the structure was rhombohedral.
The \( \beta \) phase was found to be continuous from 45 to 55% Sb with the following lattice parameter measurements.

\[
\begin{array}{ccc}
45\% \text{ Sb} & a = 6.117 \, \text{Å} & \alpha = 89.7^\circ \\
52.4 \text{ "} & a = 6.124 \, \text{Å} & \alpha = 87.3^\circ \\
55 \text{ "} & a = 6.138 \, \text{Å} & \alpha = 89.18^\circ
\end{array}
\]

**Table 3 Lattice Constants for SbSn**

The supposed \( \beta - \beta^1 \) transformation revealed by thermal analysis was studied by reheating alloys to 350°C (30°C above the transformation temperature) followed by rapid quenching. The structure so obtained was identical to the room temperature structure. From this it was concluded that either the change was due to an order/disorder transformation in the rhombohedral structure, or that the high temperature structure might be an undistorted NaCl type which even rapid quenching was unable to retain.

An order/disorder transformation was also proposed by Iwase et al.\(^{(16)}\), but the thermoanalytical results of Predel and Schwermann\(^{(21)}\) indicated an intermetallic phase of composition \( \text{Sn}_3\text{Sb}_2 \). This was formed on cooling by a peritectic reaction between the melt and the \( \beta \) phase at 324°C and which decomposed at 242°C into the \( \beta^1 \) phase containing 43 at \% Sb and tin solid solution containing 9.4% Sb.
The exact composition of this phase, which was stable in this narrow temperature interval, was obtained by quantitative evaluation of the thermal effect at 324°C. At 40 wt% Sb a maximum heat evolution was obtained in agreement with the results of Iwase\(^{16}\). The possibility of the peritectic formation of a phase at 321°C was also discussed by Stegher\(^{23}\), but was held to be incompatible with his x-ray results.

### 2.1.2 The Tin-Copper Equilibrium Phase Diagram

Although the copper-tin diagram is well known, the tin rich end has received little examination. Copper has an extremely small solubility in tin, and forms a eutectic between the solid solution and the intermediate \(\eta'\) phase (Cu\(_6\)Sn\(_5\)).

Investigations by Gurevich and Hromatako\(^{24}\), Haughton\(^{25}\) and Hanson, Sandford and Stephen\(^{26}\) have given the following values for the eutectic composition and temperature, and also the maximum solid solubility.

<table>
<thead>
<tr>
<th>Maximum Solubility</th>
<th>Eutectic Composition</th>
<th>Temperature</th>
<th>Reference</th>
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</thead>
<tbody>
<tr>
<td>-</td>
<td>1%</td>
<td>227.1°C</td>
<td>24</td>
</tr>
<tr>
<td>0.2%</td>
<td>1%</td>
<td>227.4°C</td>
<td>25</td>
</tr>
<tr>
<td>&lt;0.01%</td>
<td>0.7 - 0.75%</td>
<td>226.9°C</td>
<td>26</td>
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</table>

Table 4 Phase Diagram results for Sn-Cu alloys
A different type of investigation was carried out by Homer and Plummer (27) who were studying the high temperature brittleness of tin containing small amounts of impurities. This they attributed to the incipient melting of small quantities of eutectics. By lightly loading the testpiece in bending, and slowly increasing the temperature, intercrystalline failures were obtained at the exact melting points of the eutectics concerned. For the copper-tin eutectic temperature they obtained 226.6°C by this method against 226.9°C obtained by Hanson, Sandford and Stephens. This technique was extended to alloys of very low copper contents to determine the solidus of hypoeutectic alloys, and hence find the limit of solid solubility at the eutectic temperature.

Annealed specimens were produced containing 0.001% - 0.006% Cu. These all gave definite fractures exhibiting a very large grain size. The results are shown below in figure 2.

![Fig 2 Fracture temperature of Sn-Cu alloys](image-url)
The specimen containing 0.0058% Cu failed at 227°C, and this seemed to be almost exactly the limit of solubility at the eutectic temperature. The solidus line cuts the eutectic line at 0.0063% Cu.

A further check on the experimental method was made by repeating the tests using a sample of super-purity tin (2 ppm impurities). This was found to be soft and plastic up to 232°C when it failed. Fusion had occurred at the point of failure, and elsewhere, and no sign of intercrystalline fracture could be seen. Despite the problems inherent in this method the authors have achieved a large measure of self-consistency and obtained good agreement with determinations by other methods, so that the value of 0.006% Cu for the limit of solid solubility at the eutectic temperature appears to be the most accurate value available. The general form of the whole phase diagram is shown below.
2.1.3 The Ternary System Sn-Sb-Cu

Bonsack\(^{28}\) examined the structure of as-cast alloys, and found no ternary intermediate phase, but he indicated that solid alloys in the tin-rich corner were contained by the triangle Sn–\(\beta\)–\(\ell\).

Ellis and Karelit\(z^{30}\) studied tin-rich alloys only, and determined the liquidus and solidus surfaces. Their results are in good agreement with the work of Tasaki\(^{29}\).
who investigated the entire ternary system, and constructed a satisfactory qualitative model. In the tin rich corner he found an invariant reaction at 240°C between liquid, $\eta'$ ($\text{Cu}_6\text{Sn}_5$), $\beta$ (SbSn) and tin rich solid solution, but did not give the composition of the phases involved, nor the equilibrium reactions in the solid state. Tasaki identified one ternary compound metallographically as $\text{Cu}_{12}\text{Sn}_7\text{Sb}_3$, and also indicated that the solubility of antimony in $\text{Cu}_6\text{Sn}_5$ decreased with temperature.

Harding and Pell-Walpole have made a careful study in the region up to 14% antimony and 3% copper. The room temperature section through their diagram is shown in fig. 4.

![Figure 4](image)

*Figure 4*

*The Tin Rich Corner of the Sn-Sb-Cu Phase Diagram*
As can be seen the ternary alloys are mixtures of the phases found in the binary systems, with no ternary compounds in the range of compositions under study. Owing to the relatively small amount of $\eta'$ at the eutectic composition the compound rarely shows the typical eutectic structure, but consists of isolated particles of $\eta'$ in a cored $\alpha$ matrix. In hypereutectic alloys the $\eta'$ forms as needles, prisms, or star like crystals in the $(\alpha + \eta_1)$ matrix.

No attempt was made to verify the binary portions of the diagram since the results of Hanson and Pell-Walpole and Homer and Plummer were accepted for the Sn-Sb and Sn-Cu binary equilibrium. However, a more accurate diagram would be obtained if the size of the $(\alpha + \eta_1)$ phase field were reduced to take account of the more recent work by Eyre on the limit of solid solubility of antimony in tin.

Summary of constitution (2.1.4)

The question of the number and nature of intermediate phases present in the tin-antimony system is one that concerned early workers for several years. Clearly they were hampered in their investigations by the lack of high purity metals, and measuring instruments that were in a low state of development.
The more recent investigations employing x-ray diffraction all agree that there is only one intermediate stable phase present. This is the rhombohedral SbSn compound \( \beta \), with a wide range of homogeneity from 42 to 57% Sb rather than a \( \text{Sn}_4\text{Sb}_3 \) or \( \text{Sn}_4\text{Sb}_5 \) phase. Transformations near the low antimony \( \beta \) phase boundary at approximately 325°C are still not clearly understood. It has been speculated that this may be an order/disorder transformation and both Iwase and Bowden stated that high temperature x-ray diffraction was in progress. Unfortunately no results have been published, nor does the technique appear suitable for resolving the question since the atomic scattering factors of tin and antimony are so similar that the observation of superlattice lines is unlikely.

Predel and Schwermann deny the existence of an order/disorder transformation and attribute thermal effects within the \( \beta \) phase to lack of specimen homogeneity. Thermal effects at 40% Sb, and double arrests on cooling at 250°C and 242°C between 10% Sb and 40% Sb are attributed to the formation of an \( \text{Sn}_3\text{Sb}_2 \) phase. The existence of this phase is in complete agreement with their experimental results, but has not been positively identified by x-ray diffraction.
The work by Eyre on the limit of solid solubility of antimony in tin is difficult to refute and shows good agreement with Hanson and Pell-Walpole at higher temperatures. Earlier figures of 8 - 10% antimony at room temperature seem to be based on the first appearance of SbSn cuboids rather than the very fine precipitates formed at grain boundaries, and therefore do not represent the equilibrium solubility. In this system microscopic methods are to be preferred to the use of x-ray parameter measurement since the change in parameter is small and supersaturation difficult to avoid.

The tin-copper system has been shown to have a eutectic at approximately 0.75% Cu, and a very small solubility for copper. This is less than 0.01% and probably 0.006%. Both of these figures refer to 220°C, the room temperature solubility being even less.

None of the ternary diagrams can be reconciled with the tin-antimony binary diagram at room temperature. Harding and Pell-Walpole's diagram appear quite reasonable at 200°C, but at 20°C the \( \alpha + \eta^1 \) phase field should be restricted to 0.7% antimony to agree with the work of Eyre rather than extending to 2\( \frac{1}{2} \)% Sb as published.
2.2 Diffusion and the Achievement of Equilibrium

The rates of tin self diffusion, grain boundary diffusion, and the matrix diffusion rates of antimony in tin, have been studied by several authors. The most recent investigations show results consistent with earlier work, and these are summarised below.

**Tin, self diffusion, single crystals:**

Ref: Huang and Huntington \(^{(32)}\)

\[
D \parallel 'c' \text{ axis } = 12.8 \exp\left(-\frac{26}{RT}\right) \text{ k cal/mole}
\]

\[
D \perp 'c' \text{ axis } = 21.0 \exp\left(-\frac{25.2}{RT}\right) \text{ k cal/mole}
\]

**Tin, self diffusion, polycrystalline material**

Ref: Lange et al \(^{(33)}\)

\[
D = 0.78 \exp\left(-\frac{22.8}{RT}\right) \text{ k cal/mole}
\]

**Tin, grain boundary diffusion**

Ref: Lange \(^{(34)}\)

\[
D = 6.4 \times 10^{-2} \exp\left(-\frac{9.55}{RT}\right) \text{ k cal/mole}
\]

**Antimony in Tin, matrix diffusion**

Ref: Huang and Huntington \(^{(32)}\)

\[
D \parallel 'c' \text{ axis } = 71 \exp\left(-\frac{29}{RT}\right) \text{ k cal/mole}
\]

\[
D \perp 'c' \text{ axis } = 73 \exp\left(-\frac{29.4}{RT}\right) \text{ k cal/mole}
\]

In contrast with the low diffusion rates typical of substitutional solutes, some metals including Au, Ag, Cu and Zn diffuse at extremely fast rates, particularly in the 'c' direction.

Dyson et al \(^{(37)}\) reported results for the mobility of copper in 'c' and 'a' oriented tin single crystals.
The diffusivity of copper in the 'a' direction was found to be:

\[ D \parallel 'a' = 2.4 \times 10^{-3} \exp \left( \frac{-7.9}{RT} \right) \text{k cal/mol} \]

The mobility of copper in the 'c' direction was found to be extremely rapid. An approximate value of \( 2 \times 10^{-6} \text{Cm}^2/\text{sec} \) was obtained at 25°C, which was approximately 500 times the diffusivity in the 'a' direction. The activation energy in the 'c' direction was 4 k cal/mole assuming \( D_0 \approx 10^{-3} \text{Cm}^2/\text{sec} \). Behaviour of this type was considered to be due to interstitial diffusion rather than relying on a vacancy mechanism.

2.2.1 Discussion of diffusion literature

The results of Huang and Huntington\(^{(32)}\) for single crystals (26 k cal/mole) compare well with those of Lange et al\(^{(33)}\) for polycrystalline tin (22.8 k cal/mole). The latter result shows a slightly lower activation energy as would be expected since grain boundary diffusion would make some contribution to the overall diffusion rate. Lange\(^{(34)}\) has measured a value of 9.55 k cal/mole for this latter process, which is somewhat lower than the value of half the single crystal matrix diffusion energy frequently observed in other metals.

The activation energies for the matrix diffusion of antimony in tin and tin self diffusion are similar, and it may be concluded that the diffusivities in both cases are controlled by the same vacancy diffusion mechanism.
Dramatically smaller values are obtained for the diffusion of copper and certain other metals in tin, typified by the work of Dyson et al. Activation energies of 8 k cal/mole in the 'a' direction and approximately half this amount in the 'c' direction are clearly incompatible with a vacancy diffusion mechanism, and hence also incompatible with a substitutional solid solution. Instead it was proposed that diffusion is achieved by an interstitial mechanism, and that the copper atom describes a spiral path as it passes down the 'c' axis from one interstitial position to another. None of the authors comment on the exact nature of the diffusion mechanism in the 'a' direction. Whilst the activation energy is approximately twice that in the 'c' direction it is still far lower than that expected for vacancy diffusion, and it must be speculated that this reflects the increased difficulty of interstitial diffusion in a more closely packed direction.

2.3 Mechanical properties of Pewter Alloys

Several investigators have studied the changes that take place in the mechanical properties of Pewter when it is deformed, usually by carrying out hardness measurements, although tensile and bend tests have also been used.
In many instances however, it is not possible to compare the results of different investigations since the properties were measured under a variety of non standard conditions.

The hardness of cast pewter has been reviewed by the Tin Research Institute for a variety of compositions\(^{(38)}\). The results from 19 investigations have been compared, and preferred values obtained. These are shown below in table 5 and were determined under standardised conditions of Brinell hardness testing such that \(L/D^2 = 5\), and with an indentation time of 30 seconds at 20°C.

<table>
<thead>
<tr>
<th>% Sb</th>
<th>% Copper</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>5 9 10 11</td>
</tr>
<tr>
<td>2</td>
<td>10 11 12 13</td>
</tr>
<tr>
<td>4</td>
<td>14 15 16 17</td>
</tr>
<tr>
<td>6</td>
<td>16 17 19 21</td>
</tr>
<tr>
<td>8</td>
<td>20 22 23 24</td>
</tr>
<tr>
<td>10</td>
<td>23 24 25 26</td>
</tr>
</tbody>
</table>

**Brinell Hardness of Pewter Alloys\(^{(38)}\)**

**Table 5**

The effects of cooling rate on the hardness of cast ingots were studied by Thompson and Orme\(^{(39)}\), Heyn and Bauer\(^{(40)}\) and Greaves\(^{(41)}\). In all three cases it was found that alloys quenched from near the melting point were slightly harder than those which had been slowly cooled.
Greaves also extended his work to the effects of rolling on the hardness of pewter, and obtained the following Brinell hardness using a 500 kg load and 10 mm ball for 60 seconds. (Table 6)

<table>
<thead>
<tr>
<th>Composition</th>
<th>5% Sb</th>
<th>5% Sb/0.8% Cu</th>
<th>5% Sb/1.5% Cu</th>
</tr>
</thead>
<tbody>
<tr>
<td>As Cast</td>
<td>14.3</td>
<td>18.3</td>
<td>21.6</td>
</tr>
<tr>
<td>Rolled 47%</td>
<td>11.0</td>
<td>16.8</td>
<td>16.0</td>
</tr>
<tr>
<td>Rolled 60%</td>
<td>9.7</td>
<td>12.4</td>
<td>11.0</td>
</tr>
<tr>
<td>Rolled 60%</td>
<td>-</td>
<td>12.4</td>
<td>11.5</td>
</tr>
</tbody>
</table>

Table 6 Brinell Hardness Results for Rolled Pewter

It was commented that the effects of rolling were far more pronounced than any variation due to the cooling rate during casting. In all cases the alloys softened on rolling, and the greater the deformation, the greater was the hardness loss.

A similar investigation was carried out by Edgeberg and Smith using alloys containing approximately 7% antimony and 2% copper. In addition to Brinell hardness tests a shore Scleroscope fitted with a magnifying hammer was used to determine hardness, the results of which are shown in table 7.
<table>
<thead>
<tr>
<th>% Deformation</th>
<th>0</th>
<th>50</th>
<th>66</th>
<th>75</th>
<th>83</th>
<th>91</th>
<th>93</th>
</tr>
</thead>
<tbody>
<tr>
<td>Brinell Hardness</td>
<td>23.8</td>
<td>19.7</td>
<td>18.6</td>
<td>17.2</td>
<td>15.9</td>
<td>13.3</td>
<td>-</td>
</tr>
<tr>
<td>Scleroscope Hardness</td>
<td>10</td>
<td>14</td>
<td>14</td>
<td>15</td>
<td>15</td>
<td>16</td>
<td>21</td>
</tr>
</tbody>
</table>

Table 7 Hardness Results for Rolled Pewter

It can be seen that the Brinell hardness falls with deformation, whilst the Scleroscope hardness does the opposite. It was concluded by the authors that these results were erroneous, and that the Scleroscope was unsuitable for testing these materials, however the implications of these results will be discussed in section 5.4.

A further paper by the same authors contained more hardness data, but unfortunately these did not correlate with their previous results, nor with any other investigations. There was no comment as to this apparent anomaly.

Similar work was carried out by Karelitz and Ellis on a number of tin-antimony-copper alloys. They used an unusual method of testing, loosely based on a Rockwell hardness test, but found a general trend that alloys with high antimony and copper contents softened more on rolling than alloys with lower amounts of alloying additions.

A major investigation into the effect of cold work on the hardness of Pewter was made by Leyman in 1937. He studied the properties of a range of alloys containing up to 7.3% antimony and 3% copper which had received deformations in the range of 0 - 80%.
Phantoms give less redundant work. Hardness maximum at Page 2. R clandestine.
Alloys were prepared from Chempur tin (99.99%), Cookson's antimony (99.7%) and electrolytic copper, and the ingots rolled by hand between steel sheets at a maximum reduction of 1% per pass. Brinell hardness tests were carried out using a 5kg load and a 2mm ball, and the results of these tests can be seen in figs 5 - 7.

Tin antimony alloys hardened at first on cold rolling, the maximum hardness being reached at 40 - 50% reduction. Further working caused progressive softening until at 80% reduction the hardness was approximately equal to or less than in the cast condition. An increase in the antimony content gave a higher cast hardness and an increased tendency to soften on severe cold working.

Alloys containing copper were harder than the binary tin-antimony alloys of the same antimony content. It was noticed, however, that an increase in copper content from 0.5% to 0.96% had no appreciable effect on the hardness of the alloy in the cast or rolled condition. Up to about 20% reduction the hardness increased, and on further working decreased again. The alloy containing 2.86% copper was harder than the two alloys of lesser copper content in the cast condition. Rolling, however, caused a much greater softening in this alloy, and at 80% reduction it was softer than any of the binary or ternary alloys.
Effect of cold rolling and annealing on the hardness of an alloy containing 3.18% Sb.

Effect of rolling and annealing on the hardness of an alloy containing 5.15% Sb.
Effect of cold rolling and annealing on the hardness of an alloy containing 7.28% Sb.

Effect of cold rolling and annealing on the hardness of an alloy containing 5.09% Sb. and 0.5% Cu.
Effect of cold rolling and annealing on the hardness of an alloy containing 4.58% Sb. and 0.96% Cu.

Effect of cold rolling and annealing on the hardness of an alloy containing 4.56% Sb. and 2.58% Cu.
It was considered that the fall in hardness on working to a value below that of the cast alloys was due to precipitation of the SnSb (p) phase, the solid solution being weakened.

Microscopy showed a distorted cold worked structure up to 40% deformation in an alloy containing 3.18% Sb. After 50% reduction evidence of recrystallisation could be seen. This took place quite rapidly at room temperature when the recrystallisation temperature was decreased by the large amounts of cold work present.

Homer and Plummer (29) determined the hardness and tensile strengths of a series of annealed alloys containing 3, 7 and 10% antimony. These gave tensile strengths of 27.8, 50.9 and 71 Megapascals whereas the Brinell hardnesses were 8.7, 14.4 and 17.3 respectively, i.e. the tensile strengths increased more rapidly with antimony additions than did the hardness.

Hanson and Pell-Walpole (46) made an extensive investigation of the mechanical properties of tin-antimony alloys containing up to 18% Sb. It was found that the Brinell hardness and tensile strengths in the cast condition increased linearly between 0 and 10% Sb. Alloys containing more than 10% Sb showed a more gradual improvement in strength due to the formation of SbSn cuboids.
If chill cast specimens were annealed at 225°C and furnace cooled, a small decrease in strength and hardness was observed (~2 BHN). This was attributed to the slowly cooled alloys being closer to equilibrium conditions and having a lower supersaturation of antimony in solid solution.

Alloys were also rolled between 0 and 80% deformation. The results obtained were similar to those reported by Leyman.

During aging at room temperature no further softening occurred with alloys that had been reduced 10 - 30%, but with larger reductions softening occurred during the first 20 days, and then at a much slower rate until 70 - 100 days after rolling. After this time the hardness of specimens in the deformation range 35 - 60% reached stable values, but those rolled in excess of 65% continued to soften gradually for at least 6 months. The lowest hardness recorded was 12 BHN for the 80% reduced specimen.

The authors considered that softening occurred by self annealing, either during the cold working process or on subsequent standing. This was accomplished by a breakdown of the original grain structure and may result in complete recrystallisation at room temperature. The new grains were extremely small since appreciable grain growth could not occur at room temperature.
Thus, apart from the original work hardening which occurred with small amounts of cold work, each subsequent change in Brinell hardness was accompanied by a change in grain size.

A recent study on the effect of rolling on the properties of pewter has been made by Arumini and Baroni\(^{(47)}\). They were not concerned with the softening that occurs on rolling, but studied the anisotropy found in rolled sheet. A 5% Sb, 1% Cu, 0.15% Cadmium alloy was used and reduced 96% by unidirectional rolling. This was then tensile tested in various directions and the following results obtained.

<table>
<thead>
<tr>
<th>Angle to Rolling Direction</th>
<th>U.T.S. MPa</th>
<th>Yield Stress MPa</th>
<th>Elongation %</th>
</tr>
</thead>
<tbody>
<tr>
<td>0°</td>
<td>70</td>
<td>60</td>
<td>57</td>
</tr>
<tr>
<td>45°</td>
<td>60</td>
<td>52</td>
<td>88.5</td>
</tr>
<tr>
<td>90°</td>
<td>71</td>
<td>60</td>
<td>53</td>
</tr>
<tr>
<td>135°</td>
<td>59</td>
<td>52</td>
<td>81</td>
</tr>
</tbody>
</table>

Table 8 Anisotropic Properties of Rolled Pewter

This is an unusual composition for Pewter since cadmium is not permitted as an alloying addition for pewter due to its toxic nature.

Duckett and Ainsworth studied the factors affecting the directional properties of rolled pewter sheet, and also determined the hardness of a 6% Sb, 2% Cu alloy as a function of rolling reduction\(^{(48)}\). The alloy had been rolled and heat treated for 30 mins. at 180°C prior to re-rolling, but the results compare well with previous investigations using
cast ingots as a starting material.

2.3.1 The Effect of Heat Treatment on Rolled Pewter

The hardening effect of heat treatment on rolled pewter has been known to craftsmen pewterers from antiquity. They found that heating spun pewterware to near its melting point followed by air cooling restored the metallic ring when struck, and gave an article of greater strength and rigidity.

One of the first scientific investigations of this treatment was carried out by Greaves, who used alloys containing 5% Sb and additions of 0.8 and 1.5% Cu. These were reduced 60% by rolling followed by an annealing treatment and gave the following Brinell hardnesses (table 9).

<table>
<thead>
<tr>
<th>Treatment</th>
<th>5% Sb</th>
<th>5% Sb/0.8% Cu</th>
<th>5% Sb/1.5% Cu</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rolled 60%</td>
<td>9.7</td>
<td>12.4</td>
<td>11.0</td>
</tr>
<tr>
<td>Rolled 60% + 1 hour</td>
<td>10.3</td>
<td>13.4</td>
<td>12.5</td>
</tr>
<tr>
<td>Rolled 60% + 1 hour</td>
<td>13.9</td>
<td>16.7</td>
<td>17.5</td>
</tr>
</tbody>
</table>

Table 9 Effect of Heat treatment on Rolled Pewter

The hardening produced by heating to 100°C is small, but heat treatment at 200°C results in a hardness increase to near the cast value. No comment was made concerning the mechanism of hardening.
Egeberg and Smith made a more extensive study of the effect of heat treatment using a variety of temperatures and initial reductions\(^{(42)}\). The alloy contained 7% antimony and 2% copper, and the following results were obtained.

<table>
<thead>
<tr>
<th>Reduction %</th>
<th>0</th>
<th>50</th>
<th>66</th>
<th>75</th>
<th>83</th>
<th>91</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cold Rolled</td>
<td>23.8</td>
<td>19.7</td>
<td>18.6</td>
<td>17.2</td>
<td>15.9</td>
<td>13.3</td>
</tr>
<tr>
<td>30 mins</td>
<td>22.8</td>
<td>20.1</td>
<td>18.2</td>
<td>17.2</td>
<td>16.8</td>
<td>14.8</td>
</tr>
<tr>
<td>90 mins</td>
<td>22.8</td>
<td>19.3</td>
<td>17.8</td>
<td>18.6</td>
<td>17.8</td>
<td>17.2</td>
</tr>
<tr>
<td>45 mins</td>
<td>22.8</td>
<td>19.7</td>
<td>20.1</td>
<td>20.1</td>
<td>20.1</td>
<td>18.6</td>
</tr>
<tr>
<td>30 mins</td>
<td>22.8</td>
<td>20.9</td>
<td>20.9</td>
<td>20.9</td>
<td>20.5</td>
<td>19.3</td>
</tr>
</tbody>
</table>

Table 10  **Effect of Heat Treatment on the Hardness of Rolled Pewter**\(^{(42)}\).

The authors considered that "only the most deformed crystals recrystallised at the lower temperature, a property that explains the fact that a steady increase in hardness is found within the same sample when it is subjected to a rising temperature." None of the specimens were examined metallographically, so they must have associated the start of recrystallisation with a significant increase in hardness. This is not a reasonable assumption as will be seen from subsequent papers from other investigators.

In a later paper by the same authors they concentrated more on the metallography of rolled and heat-treated alloys.\(^{(43)}\)
It was found that below 40% reduction the grain structure of the material was easily visible, but at greater reductions they were unable to see the grain boundaries.

The heat treated samples all showed a recrystallised grain structure, and contained less of the white constituent (SbSn) than in the corresponding samples before heat treatment. They assumed that the increased strength and hardness brought about by heating was due to resolution of the SbSn. Conversely the weakening of samples cold rolled to more than 40% might be due partly to the precipitation of SbSn.

Leyman has studied the effects of heat treatment, and also aging at a variety of temperatures, on the hardness of a number of Tin-Antimony and Tin-Antimony-Copper alloys. He found that rolled Sn-Sb alloys when annealed at 100°C for 3 hours had little change in their hardness, but higher annealing temperatures brought all specimens to about the same hardness as when cast. Increase in antimony content appeared to increase the tendency to soften on severe cold working, and to recover hardness on subsequent annealing. Samples which had been lightly deformed, and had a cold worked structure were partly or completely recrystallised as a result of the heat treatment, the degree of recrystallisation depending on the temperature used.
100°C for 3 hours resulted in slight recrystallisation of the 30% deformed sample, and a greater amount in one deformed by 50%. Annealing at 200°C for 3 hours was sufficient to cause complete recrystallisation after 20% reduction.

Sn - Sb - Cu alloys containing up to 1% copper resembled the binary tin-antimony alloys in their behaviour.

An alloy containing 4.66% Sb and 2.86% Cu behaved quite differently from the tin-antimony alloys when rolled and annealed. While annealing softened the specimens with a reduction of up to 40%, those rolled to greater deformations were hardened. The amount of hardening increased with increasing annealing temperatures, and was greatest for the specimens which had been most severely worked, and hence softened the most beforehand. None of the annealed specimens, however, were quite as hard as they were in the cast condition. These results are in good agreement with those of Egeberg and Smith\(^{(42)}\) for an alloy containing 7% Sb and 2% Cu.

After annealing some of the specimens were water quenched from 200°C and aged at 20°C, 100°C and 180°C. The various aging treatments had no appreciable effect, the hardness figures obtained being within one Brinell unit of those specimens annealed at 200°C and air cooled.
Photomicrographs of the annealed 3.18% Sb alloys show complete resolution of the $\beta'(\text{SbSn})$ phase at 200°C with a fully recrystallised matrix. The grain size is very much larger than the same specimen in the rolled condition.

Hanson and Pell-Walpole\(^{(46)}\) found that annealing deformed Sn-Sb alloys at 225°C caused their hardness to increase to a value which was approximately that of the chill cast alloy, in agreement with the work of Leyman.

The restoration of rolled alloys to their cast hardness by annealing at 150 - 225°C was observed by Schwartz and Summa for an alloy containing 8% Sb.\(^{(18)}\) They attributed this to the precipitation of the $\beta'$ phase during annealing. This explanation is contrary to the work of all other investigators, particularly Leyman, who found the phase to be precipitated during deformation and redissolved on annealing. No metallography was carried out on the alloys in question, reliance being placed on some x-ray results. There was no discussion as to why their conclusions were directly opposed to the findings of other investigators.
2.3.2 Creep Properties of Tin and Pewter Alloys

Most metals when they are worked or tested at a temperature in excess of half the absolute melting temperature have a creep component in their deformation behaviour. In many of the papers concerning the mechanical properties of pewter little attention has been paid to the rate of testing, or the indentation times of hardness tests. It has been shown by Murty et al\(^{49}\), that the size of a hardness impression is a function of time where creep is significant. Also it is possible to evaluate steady state creep parameters such as the stress exponent\(n\) and activation energy \(Q\) from hardness tests carried out over a range of indentation times and temperatures.

Murty et al\(^{49}\), using Atkins' analysis of the stresses acting on the surface of a metal subjected to spherical indentation\(^{50}\) has shown that the diameter of indentation can be expressed by the equation:

\[
\log d = A_2 - \left( \frac{1}{2n-1} \right) \frac{Q}{RT} + \left( \frac{1}{2n-1} \right) \log (t + a)
\]

Where \(d\) = indentation diameter

\(A_2\) and \(a\) are constants

\(n\) = stress exponent

\(Q\) = Activation Energy
Thus a plot of log $d$ vs log $t$ from the data obtained at constant load and temperature should be linear at longer times ($t \gg a$), and its slope will be $(\frac{1}{2n-1})$. Hence the value of the stress exponent ($n$) may be obtained.

This treatment is derived for spherical indentation, but it has been shown experimentally by Atkins that it is valid for a variety of indenter shapes and may be safely extended to Vickers pyramids.

The change in indentation diameter with time has been used by Hargreaves\(^5\) to study the effect of deformation on tin and a number of low melting point metals, their dilute alloys and eutectics. He suggested an equation of the form $d = ct^s$, where $c$ and $s$ are non-constant factors. This equation has, however, a number of short-comings as shown by Fell\(^5\), since a fit is only obtained over limited testing conditions, and the data is more easily interpreted by the treatment of Murty\(^9\).

Tensile creep tests have been carried out on tin and several of its alloys by Hanson and Sandford\(^5\,^3\,^4\). It was found that the addition of 1% Sb gave a significant improvement in the creep properties, extending the time to rupture from 79 days to 3 years at 2.76 MPa. Additions of antimony and cadmium together produce much greater improvements, and after cold rolling and self annealing an alloy with 7% Cd and 9% Sb withstood a stress of 8.3 to 9.67 MPa for many years.
No secondary creep rates were given for any of these alloys.

The activation energy for the creep of tin has been determined by Breen and Weertman\(^{(55)}\) using long term hardness tests. Values of 13 -14 K cal/mole were obtained for polycrystalline specimens between 273 and 393°K.

Another determination by Frenkel, Sherby and Dorn\(^{(56)}\) using tensile creep tests on annealed high purity tin gave a value of 21+2 k cal/mole. This is in quite good agreement with the results of Huang and Huntington for the activation energy for tin self diffusion (26 K cal/mole), and is to be preferred since the results of Breen and Weertman would indicate an inconsistency between the activation energies for creep and self diffusion not found in other metallic systems.

2.4 "Work softening" in other systems and its relation to superplasticity.

The reduction in indentation hardness after deformation is not confined to alloys containing tin and antimony, but is also found in a number of low melting point eutectics. Hargreaves\(^{(57)}\) studied the effects of deformation on a number of eutectics, and presented the following results determined under standardised conditions of testing.

<table>
<thead>
<tr>
<th>Material</th>
<th>Cast Hardness</th>
<th>Deformed Hardness</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sn - Pb eutectic</td>
<td>14 B.H.N.</td>
<td>4.2 B.H.N.</td>
</tr>
<tr>
<td>Cd - Zn</td>
<td>32 &quot;</td>
<td>22 &quot;</td>
</tr>
<tr>
<td>Sn - Zn</td>
<td>22 &quot;</td>
<td>14 &quot;</td>
</tr>
<tr>
<td>Sn - Cd</td>
<td>15 &quot;</td>
<td>9 &quot;</td>
</tr>
</tbody>
</table>

Table 11 Brinell Hardness of Eutectics.
All the eutectics studied decreased their hardness with deformation. Annealing the deformed material at 175°C caused a return to the cast hardness in alloys strained by 26.5% or less, whilst alloys that had received a larger deformation were hardened to a lesser extent.

In a later paper the effects of progressive deformation were studied in the Sn-Ag, Sn-Cu and Pb-Au eutectics as well as a lead 14% tin alloy. The results are shown below.

<table>
<thead>
<tr>
<th>Reduction %</th>
<th>Sn - Ag</th>
<th>Sn - Cu</th>
<th>Pb - Ag</th>
<th>Pb/14% Sn</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>14.5</td>
<td>15.4</td>
<td>11.0</td>
<td>12.8</td>
</tr>
<tr>
<td>10</td>
<td>14.2</td>
<td>17.0</td>
<td>12.5</td>
<td>12.8</td>
</tr>
<tr>
<td>23</td>
<td>14.1</td>
<td>16.5</td>
<td>12.6</td>
<td>12.5</td>
</tr>
<tr>
<td>35</td>
<td>13.8</td>
<td>15.0</td>
<td>12.6</td>
<td>11.8</td>
</tr>
<tr>
<td>50</td>
<td>13.1</td>
<td>13.2</td>
<td>12.6</td>
<td>11.1</td>
</tr>
<tr>
<td>70</td>
<td>12.7</td>
<td>11.8</td>
<td>12.5</td>
<td>8.8</td>
</tr>
<tr>
<td>80</td>
<td>12.5</td>
<td>10.8</td>
<td>11.9</td>
<td>-</td>
</tr>
</tbody>
</table>

Table 12: The effect of Progressive Deformation on Hardness of various eutectics

In 1929 Hargreaves interpreted these results in terms of his theory of Intercrystalline Cohesion\(^{(58)}\), although today they would be recognised as aspects of superplasticity.

From reviews of the literature by Davies et al\(^{(59)}\) and Edington et al\(^{(60)}\) it is clear that structural superplasticity has been observed in a large range of two phase alloys, many of which are based on eutectic or eutectoid compositions, although it has been demonstrated that relatively pure metals
can also behave superplastically under certain conditions. Most superplastic materials exhibit a sigmoidal variation of $\log \sigma$ with $\log \dot{\varepsilon}$, the region of maximum strain rate sensitivity with slope of $m > 0.3$ delineates the strain rate range over which superplasticity occurs.

A large number of experiments have been carried out in this area, but they have not produced results which define a unique rate controlling mechanism, however the most viable models are those which involve grain boundary sliding in association with some accommodation mechanism to achieve compatibility at grain boundaries\(^\text{51}\). The different models are:

1) A combination of grain boundary sliding and diffusion creep.

1\text{I}) A combination of grain boundary sliding and grain boundary migration.

1\text{II}) A multiple combination of grain boundary sliding, grain boundary migration and localised dislocation motion by glide and/or climb.\(^\text{66,67,68}\)

For these processes to take place a number of important criteria must be met. Firstly the material must have a fine equiaxed grain size ($< 10\mu m$) which remains stable during deformation. This is frequently obtained by heavily hot working two phase alloys where the phases are present in approximately equal proportions. In general these tend to be eutectics or eutectoids, although it has been shown by several workers that two phase alloys where one phase pins the grain boundaries of the other are also effective at stabilising the grain size as to produce superplasticity. \(^\text{69,70}\)
If grain growth occurs during the test, or if the grains do not remain equiaxed the ability to show superplasticity is lost. Secondly the strain rate sensitivity index of the material should be high \((m > 0.3)\), compared with values of \(\approx 0.1\) for conventional plasticity. It has been found that the value of \(m\) varies with grain size, temperature of deformation, and strain rate.

There is some indication that the diffusion rates in both phases of duplex alloys should be similar at the deformation temperature if superplasticity is to take place. There is, however, some degree of uncertainty as to whether this point is a necessary condition for superplasticity.

These observations suggest that the eutectics studied by Hargreaves (57, 58) deform partly by a grain boundary process when tested in the soft, heavily worked state. In the case of cast alloys this mechanism is unavailable.

2.5 The Effect of Alloying Additions on Tin-Antimony Alloys

This section is restricted to reviewing the effect of certain alloying additions on the mechanical properties of tin-antimony alloys with a view to improving the as worked hardness. Whilst some other tin rich binary alloys have attractive properties their hardness is insufficient for a commercial replacement of existing compositions, and a complete review is beyond the scope of this report.
Leyman studied the mechanical properties of a range of tin-antimony - silver alloys containing 7 - 7½% antimony and 0 - 3% silver. These alloys resembled the binary tin-antimony alloys in their general reaction to working and annealing, but in all cases the silver caused an increase in the cast hardness.

Table 13  Effect of Deformation on the Hardness of Sn - Sb - Ag Alloys

<table>
<thead>
<tr>
<th>Material</th>
<th>As. Cast</th>
<th>80% deformation</th>
</tr>
</thead>
<tbody>
<tr>
<td>7.28% Sb</td>
<td>15.8 B.H.N.</td>
<td>13.8 B.H.N.</td>
</tr>
<tr>
<td>7.36% Sb 0.52% Ag</td>
<td>20.2 &quot;</td>
<td>15.1 &quot;</td>
</tr>
<tr>
<td>7.4% Sb 0.95% Ag</td>
<td>20.2 &quot;</td>
<td>14.2 &quot;</td>
</tr>
<tr>
<td>7.15% Sb 2.94% Ag</td>
<td>24.9 &quot;</td>
<td>16.2 &quot;</td>
</tr>
</tbody>
</table>

Whilst the cast hardness was enhanced the rate of softening increased with increasing amounts of silver. A 0.95% Ag alloy produced no increase in hardness when compared to an alloy containing 0.52% Ag, but 3% Ag showed a significant increase in both the cast and rolled hardnesses.

These alloys show worthwhile improvements in hardness over tin-antimony alloys of the same antimony content up to 80% deformation. Industrial spinning processes, however, employ larger deformations, and the high rate of softening would produce finished articles of a lower hardness than can be obtained with conventional Sn - Sb - Cu alloys.
Hanson and Pell-Walpole (17) found that cadmium caused a large increase in the hardness of tin-antimony alloys in both the rolled and cast condition. Compositions up to 14% Sb and 43% Cd were studied in the cast condition, and rolled alloys were examined in the composition range 1 - 9% Sb and 3 - 8% Cd after rolling (80% def.), and subsequent annealing at 170°C and furnace cooling. The Brinell hardness results for alloys containing 5% Sb are shown below.

<table>
<thead>
<tr>
<th>Composition</th>
<th>Chill Cast</th>
<th>Rolled 80%</th>
<th>Rolled and Annealed at 170°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>5% Sb 3% Cd</td>
<td>30.4</td>
<td>26.6</td>
<td>25.3</td>
</tr>
<tr>
<td>&quot; 4% &quot;</td>
<td>27.6</td>
<td>26.1</td>
<td>27.4</td>
</tr>
<tr>
<td>&quot; 5% &quot;</td>
<td>28.3</td>
<td>25.6</td>
<td>27.8</td>
</tr>
<tr>
<td>&quot; 6% &quot;</td>
<td>33.0</td>
<td>24.1</td>
<td>31.0</td>
</tr>
<tr>
<td>&quot; 7% &quot;</td>
<td>32.5</td>
<td>24.7</td>
<td>31.0</td>
</tr>
<tr>
<td>&quot; 8% &quot;</td>
<td>33.5</td>
<td>24.5</td>
<td>32.5</td>
</tr>
</tbody>
</table>

Table 14. Brinell Hardness of Sn-Sb-Cd Alloys

Table 14 shows that in rolled alloys the hardness is virtually independent of cadmium content. Annealing followed by furnace cooling showed little effect at 3% antimony, but gave increasing hardness as the cadmium content was increased.

All the alloys soften on rolling. Whilst tin-antimony cadmium alloys possess a useful hardness in the rolled condition, and excellent creep properties (54), the use of cadmium is not permitted in pewterware due to its toxic nature. However, it provides a good solution to the problem of hardening tin in applications where toxicity is unimportant such as white metal bearings.
Two papers in "Tin and its Uses" give information on Sn-Sb-Cu-Bi and Sn-Sb-Cu-Ag alloys\(^{(72,73)}\). Both of these alloys are soft in the rolled condition, but harden considerably when annealed at 200°C.

The bismuth containing alloy has the advantage of high hardness when heated to only 150°C, which is less than the melting point of many of the solders used in the assembly of pewterware.

<table>
<thead>
<tr>
<th>Alloy</th>
<th>As Cast</th>
<th>Rolled 90%</th>
<th>1 hr 200°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>6% Sb, 1.5% Cu</td>
<td>22.9</td>
<td>13.3</td>
<td>18.6</td>
</tr>
<tr>
<td>6% Sb, 1.5% Cu, 0.01% Ag</td>
<td>23.2</td>
<td>13.3</td>
<td>19.0</td>
</tr>
<tr>
<td>6% Sb, 1.5% Cu, 0.05% Ag</td>
<td>24.7</td>
<td>13.8</td>
<td>22.0</td>
</tr>
<tr>
<td>6% Sb, 1.5% Cu, 0.10% Ag</td>
<td>26.4</td>
<td>13.4</td>
<td>24.4</td>
</tr>
<tr>
<td>6% Sb, 1.5% Cu, 0.50% Ag</td>
<td>27.7</td>
<td>13.8</td>
<td>23.7</td>
</tr>
<tr>
<td>6% Sb, 1.5% Cu, 1.0% Ag</td>
<td>28.9</td>
<td>14.1</td>
<td>23.8</td>
</tr>
<tr>
<td>6% Sb, 1.5% Cu, 2.0% Bi</td>
<td>29.7</td>
<td>14.6</td>
<td>27.8</td>
</tr>
<tr>
<td>6% Sb, 1.5% Cu, 2.0% Bi, 0.5% Pb</td>
<td>29.8</td>
<td>*</td>
<td>-</td>
</tr>
<tr>
<td>6% Sb, 1.5% Cu, 1% Ag, 0.5% Pb</td>
<td>25.4</td>
<td>12.5</td>
<td>25.9</td>
</tr>
</tbody>
</table>

Table 15  Effect of Rolling and subsequent heat treatment on the hardness of Sn-Sb-Cu alloys containing further additions.

* Cracked on Rolling.

The alloy containing 6% Sb 1.5% Cu and 2% Bi shows the highest hardness, both as cast and after heat treatment. However, the author comments that it suffers from the tendency to crack if lead is present as an impurity. At the temperature of heat treatment these pewters are likely to take a bluish tarnish.
This can be avoided by the addition of 0.1% phosphorus during melting.

Although these compositions show excellent properties in the heat treated condition, when rolled their properties are no better than the standard pewter composition on which they are based.

Mykura studied the properties of tin-zinc and tin-zinc-antimony alloys as a function of deformation\(^{(74)}\). He obtained a combination of good ductility, a high hardness in the rolled condition and a similar colour to existing pewter. Results for the cast and rolled alloys are shown below.

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Cast Hardness</th>
<th>90% Deformed Hardness</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sn/6% Zn</td>
<td>22 H.V</td>
<td>19 H.V</td>
</tr>
<tr>
<td>Sn/6% Zn/1% Sb</td>
<td>23.5 H.V</td>
<td>23.5 H.V.</td>
</tr>
<tr>
<td>Sn/6% Zn/2% Sb</td>
<td>26 H.V.</td>
<td>23.5 H.V.</td>
</tr>
</tbody>
</table>

Table 16 Hardness of Sn/Zn/Sb Alloys

Whilst these alloys have attractive mechanical properties, some industrial producers object to the film of Zinc oxide formed on casting.
3. EXPERIMENTAL TECHNIQUES

3.1 Melting and Casting of Pewter Alloys

Pewter alloys for this investigation were cast at the works of Fry's Metals Ltd at Merton from the highest commercial quality tin.

High purity antimony and high conductivity copper were used as alloying additions in the form of crushed lumps and rolled sheet respectively.

Melting was carried out in a steel ladle coated with a wash of red lead. This prevents the dross sticking to the ladle and prevents the pick up of iron. Lead contamination from the wash is very small and does not present a problem. The tin was first melted using a butane burner and raised to 350 - 400°C with ammonium chloride as a flux and cover. Alloying additions were added to the melt, and after complete dissolution the temperature was reduced to 50°C above the liquidus (∼280°C) and the alloy cast.

Mild steel chill moulds with a wall thickness of 3/8 inch were used for casting. Sound ingots were produced with a size of 150 x 100 x 32 m.m (6" x 4" x 1 1/4") and weighing about 2 kg. This method gave ingots which were free from macro-segregation as verified by analysis of the top and bottom of the ingot. Full analyses of the alloys used is shown in Appendix 1.
In addition to tin/antimony and tin/antimony/copper alloys other experimental alloys were prepared containing additions of nickel, bismuth, antimony and zinc.

The melting and casting procedures were similar to those used for the pewter alloys except that melting was carried out in a plumbago crucible heated by three bunsen burners. High purity alloying elements were added to the molten tin in the form of crushed lumps, with the exception of nickel additions which were in the form of a 3% Ni master alloy.

3.1.2 Preparation of Ingots for Rolling

Prior to rolling, the small primary pipe was removed by cutting off the top inch of the ingot with a bandsaw. The bottom half inch was similarly removed. The chilled outer layer of the ingot was removed by milling under flood lubrication to a depth of 3.7mm on both faces that were to be rolled, to give a final thickness of 25.4mm. This preparation follows industrial practice and is designed to give a sound ingot free from surface defects.

In the later stage of the investigation ingots were homogenised before preparation and rolling. This was carried out in a salt bath at 220°C (± 2°C) for 14 days.
3.2 Rolling

Rolling was carried out on a Hille laboratory rolling mill at a speed of 7 meters/min. using 150m.m. diameter rolls. Small reductions (~0.5m.m.) were made without cross rolling, and the material was not allowed to heat up beyond room temperature. Samples were then cut from the strip at intervals of 10% reduction and prepared for hardness testing and microscopy. Ingots for the production of tensile specimens were reduced 90% by rolling to give a finished strip 2.54m.m. thick.

No difficulty was experienced in rolling the strip, with the exception of one of the development alloys, (Sn/0.3% Ni/1% Bi/1% Sb/0.5% Zn) which blistered badly due to persistent casting defects, and the 6% Sb, 2% Cu pewter alloy which showed a little edge cracking.

The rolling procedure used in this investigation departs from normal industrial practice where large reductions are employed in the initial breakdown stages, and the strip temperature frequently reaches 120°C. This modified schedule was chosen for laboratory investigation since it was considered that the high breakdown temperatures would effect the structural changes that occur in the early stages of rolling, such as causing increased precipitation or premature recrystallisation.
3.3 Preparation of Tensile Test Specimens

Tensile test specimens were obtained from 90% deformed sheet (2.54 m.m.) using a Sweeney and Blocksidge press fitted with a blanking die. The test pieces were cut such that the tensile axis was parallel to the rolling direction, and had dimensions as shown below:

![Testpiece Dimensions](image)

The specimens produced in this way showed a small amount of shearing at the edges. To determine whether this had any effect on the mechanical properties, similar specimens were prepared using an experimental router developed by I.C.I. for plastics with \(\frac{1}{4}\) H.S.S. milling cutter rotating at approximately 12,000 rpm. A clean cut edge was obtained with no evidence of distortion or plastic flow.
3.4 Determination of Hardness vs Deformation Curves

Coupons were cut from the rolled strip at intervals of 10% reduction and mounted in "Metset F.T." polyester resin. This is a cold curing resin, but exotherm temperatures of up to 100°C may be experienced with large mounts. To overcome this problem half the recommended amount of catalyst was used. This gave a cure time of about 4 hours with a maximum temperature of 30°C.

Mounted specimens were ground flat using silicon carbide papers flooded with water, and were then hardness tested using a Vickers pyramidal diamond hardness tester with a 2.5 Kg load applied for 5 seconds. Six impressions were made on each specimen, and the mean of these values used to determine the hardness.

To correlate some of the experimental values with those in the literature ball hardness tests were also carried out using a load of 125 Kg acting on a 5mm ball for 60 seconds to give a value of \( \frac{L}{d^2} \) of 5. In the absence of a suitable testing machine, a Houndsfield tensometer was used to compress the ball against the specimen.

3.5 Heat Treatment of Alloys

The heat treatment of rolled alloys was undertaken at a variety of temperatures to investigate the hardening effect of this process which is widely reported in the literature. Three alloys were used containing 2% copper with 2, 4 and 6% antimony, plus one other, containing 4% antimony and 4% copper.
The alloys were heated in an air circulating furnace at temperatures of 160°C, 180°C and 200°C for times of up to 240 hours and then air cooled to room temperature for hardness testing.

The strengthening of rolled alloys by heat treatment was also studied by tensile testing. In this case a solution treatment was given for one hour at 5°C above the α/(α + β) phase boundary. This was shown to be sufficient to obtain complete resolution of the β phase and obtain a consistent structure for subsequent testing. A salt bath filled with I.C.I. TS 150 salt was used for heat treatment due to its excellent temperature stability (± 2°C), as the solution treatment temperature for the 6% Sb alloys was very close to the melting point.

3.6 Optical Metallographic preparation

Initial preparation of samples for metallography was the same as for hardness testing. Mechanical wet grinding with silicon carbide discs was used down to 600 mesh grit, followed by diamond polishing with 6μm, 1μm. and 1/4μm paste. Considerable difficulty was experienced at first in obtaining a good polished surface. New pads of various materials were prepared, but it was found that the nap caused severe scratching, whilst the use of a very soft cloth caused excessive relief polishing.
The best solution to the problem was found to be "Microcloth" from Banner Scientific Ltd., which was satisfactory after a few hard steel specimens had been polished and worn the cloth in. Specimens of pewter polished in this way were free from surface flow and recrystallisation from polishing strains.

The final preparation of very soft specimens was by repeated polishing and etching, or by finishing on 0.3 micron alumina mixed with Teepol on Selvyt Cloth. Various etches were used to reveal the microstructure, and their effects are shown in Appendix 2. The best results were obtained with 5% Nital which darkened the tin rich solid solution, whilst the copper-tin and tin-antimony intermediate phases were unattacked and showed up as a pale straw and white colour respectively. Nital also gave good results with polarised light for enhanced grain contrast, but for best resolution of detail it was necessary to use high concentrations (5%). Etching was very rapid, taking about 3 seconds, followed by washing with methanol, as water encouraged staining.

3.6.1 Specimen Preparation for Scanning Electron Microscopy and Electron Probe Microanalysis.

Electron microscopy has been employed for the high resolution microscopy of alloys, and in conjunction with electron probe microanalysis to identify precipitates and study the antimony content of the tin rich solid solution. Alloys were examined in one or more of the following conditions:-
(1) **Clean Metal Surface.** Used for the examination of fracture surface and deformation studies in tensile specimens.

(11) **Nital Chemical Etch + Carbon Coating.** Used initially to etch away the matrix to leave precipitates in relief. This technique suffered the disadvantage of leaving a thick oxide film which interfered with analysis.

(111) **Argon Ion Sputter Etching.** As argon ions accelerated through a potential of 6KV possess considerable kinetic energy they are capable of removing tin and antimony atoms from the surface of solid specimens. The removal rates are very sensitive to the structural conditions of the surface, and this allows features such as grain boundaries, twins and precipitates to be revealed, whilst leaving a surface which is chemically clean.

An Edwards ion beam thinning apparatus type IBMA I was used with an accelerating potential of 6KV. This type of apparatus is frequently used for the thinning of non-conducting specimens from both sides for T.E.M. examination.

Using thick mounted specimens the technique was modified by sticking the mount to one of the guns with double sided Sellotape, and using the other gun facing the specimen to do the etching as shown in figure 9.
In addition spacers were placed between the specimen and the anode plate to allow the inactive gun to be evacuated with the rest of the system.

These modifications give an increase in the target to gun distance which results in a more diffuse beam arriving at the specimen. The beam was further defocused by using a large beam current of 400\(\mu\)A causing mutual repulsion of the ions, and an etched area approximately 1 cm in diameter was obtained on the specimen surface in one hour.

**Electrolytic Etching**

Electropolishing and subsequent electrolytic etching were attempted as an alternative to the above. References in the literature to suitable solutions for use with tin/antimony alloys are scarce, so a variety of electropolishing solutions suitable for tin, along with certain tin plating solutions known to produce bright anodes were tested. Most solutions gave an adherant black oxide on pewter, or produced severe pitting.
Altering the temperature, current density and voltage did not result in any significant improvement. The solutions used and their effects are shown in Appendix III.

The most successful polish/etch was based on perchloric acid in ethanol. A thick black oxide film is produced on the surface of the specimen, but with care this can be removed with cotton wool under running water to give a clean but slightly tarnished surface beneath. In this condition grain boundaries and precipitate can be clearly seen under the S.E.M.

3.6.2 Specimen preparation for Transmission Electron Microscopy

Transmission microscopy was undertaken to investigate the possible presence of very small precipitates within the matrix phase of lightly deformed pewter alloys as suggested by the unusual creep results presented in section 4.5.

Thin Foil Studies

The preparation of thin foils by the usual method of electropolishing through a thin sheet was found to be impractical with pewter since the foil was damaged by pitting and the formation of an oxide film. Instead a mechanical polishing method was employed with the full knowledge that indeterminate strains would be imparted to the foil, but hoping that some useful areas might still be obtained.

Initial preparation was carried out using a Jung Rotary microtome with a wedge steel knife to produce slices approx 10 microns thick and 5mm x 3mm in area.
Satisfactory sections could only be obtained from the soft rolled alloy, the harder solution treated material causing the knife to jam.

Microtomed slices of the 4% antimony alloy were subsequently solution treated in oil at 210°C for 2 hours to redissolve the SbSn precipitated during rolling and cutting. After treatment the foils were removed from the hot oil and washed in acetone. To reduce the foils to a usable thickness, they were fixed to a highly polished bakelite mount with Durofix adhesive and repeatedly etched in Nital and lightly polished with 0.05 micron alumina. This was carried out on both sides of the foil so as to remove the surfaces that had been in contact with the oil, until the specimen began to fragment due to most of the material having been polished away. The specimens were finally immersed in acetone for 1 hour to remove any traces of adhesive, and collected between sandwich grids for examination.

Extraction Replicas

Extraction replicas were produced to extract any fine precipitates from the tin rich matrix for T.E.M. examination.

A primary electrolytic etch was made to produce a surface in which precipitates stood out in relief using the perchloric acid/ethanol mixture described previously. After washing and drying the specimen was transferred to an Edwards vacuum coating unit where a thin layer of carbon was evaporated onto the surface. This was subsequently scored through with a scalpel to produce squares approximately 3m.m. by 3m.m.
A second etch of alcoholic ferric chloride was then used to penetrate the scores and etch underneath the carbon film which was floated off on the surface of distilled water and collected on 3mm grids. Other milder stripping etches were tested, but did not permit the removal of the film from the specimen substrate.

3.7 Quantitative Metallography

Grain size determinations were made on a series of rolled binary and ternary alloys to measure the recrystallised grain size as a function of deformation. Measurements were carried out using a Zeiss Ultraphot optical microscope at a linear magnification of 750 times on a ground glass viewing screen. Standard ASTM comparative non-ferrous grain size charts for 75 x magnification were used for measurement, and a scale factor of 10 applied to the results.

To study the changing amount of SbSn with deformation a "Quantiment" image analysis computer was used to measure the area fractions of precipitates in binary alloys. These results could then be related to volume fractions assuming spherical precipitates. Specimens for this technique were etched more heavily than usual to obtain the greatest contrast between precipitate and matrix. In addition conventional point counting was carried out using a Swift automatic point counter with a Zeiss Ultraphot microscope. The image was viewed on a ground glass screen, and 1500 points were counted for each specimen.
3.7.1 Scanning Electron Microscopy and Microprobe Analysis

Scanning Electron microscopy was carried out using either an I.S.I. "Minisem" or Cambridge Stereoscan IIA microscope on specimens prepared by methods described in section 3.6.1.

Microprobe analysis was undertaken with a J.E.O.L. J X A 50A electron probe microanalyser operated at 25KV. Analytical systems comprised a solid state Ortec energy dispersive system, and a wavelength dispersive crystal spectrometer fitted with a P.E.T. crystal for the analysis of heavier elements.

It was found that matrix analysis of a range of specimens using the W.D.S. system was exceptionally difficult due to the very long counting times required with the relatively low efficiency of the P.E.T. crystal. This in turn put a high premium on beam stability and required frequent reference to standards. As it was necessary to examine a large number of specimens the total machine time required would have been excessive, although if two W.D.S. units had been available at the time the situation would have been much improved.

As an alternative the energy dispersive analyser was used, but this suffered the disadvantage of being unable to resolve the tin and antimony Lα, emission lines as separate peaks due to the small difference in energy (3.44 and 3.605 Kev respectively).
Unresolved spectra were collected and then deconvoluted by a computer method derived by Hazell\(^{(80)}\), and shown in Appendix 4. This method compares the mean energy of the complex peak with the mean energy of the two standard peaks (Sn and Sb) which were acquired under identical conditions of counting time, beam current etc. This has the advantage over methods using a crystal spectrometer in that once the standards have been acquired, the unknown spectra can be collected under any conditions of beam current etc, since both components of the peak are collected simultaneously. Once the spectra have been deconvoluted quantitative corrections for atomic number, absorption, fluorescence and dead time are applied in the normal way using a separate standard computer programme. Check analyses were made on homogenous standards of SbSn which were previously analysed by chemical means.

Analysis was also carried out on interesting features from the extraction replicas produced for T.E.M. examination using the microprobe in the quasi-S.T.E.M. mode with a transmitted electron detector. Spectra were collected and deconvoluted as described above.

3.7.2 Transmission Electron Microscopy

Transmission electron microscopy was carried out with a J.E.O.L. JEM 100B microscope at an accelerating voltage of 100 Kv. Specimens were examined in normal transmission with the use of a goniometer stage to obtain high symmetry electron diffraction patterns.
3.8 Analysis of Pewter surfaces by Electron Spectroscopy

Surface analysis of Pewter was undertaken with a Vacuum Generators E.S.C.A. 2 photoelectron spectrometer to determine the chemical nature of the surface from which precipitates were extracted for T.E.M. examination.

This technique analyses the top few atomic layers of the specimen and is sensitive to light elements including oxygen, and can also give information about the chemical state of the analysed elements by measuring the binding energy of the ejected photoelectrons.

Specimens 8mm square were irradiated with aluminium Kα x-rays with an energy of 1486.6 eV, and the photoelectron spectra collected under ultra high vacuum conditions. Polished bulk specimens of pewter of known antimony content were used for quantitative calibration standards. All specimens were argon ion cleaned for 5 seconds to remove surface contamination from adsorbed carbon dioxide, diffusion pump vapour etc.

3.9 X-ray analysis of rolled and Heat Treated Alloys

3.9.1. Powder diffraction

X-ray powder diffraction patterns were recorded for both binary and ternary alloys. Filings were taken from freshly rolled alloys and screened at 200 mesh (74μm). Half the filings were used to produce a photograph corresponding to the heavily deformed state. The other half were sealed in an evacuated Pyrex tube and heated to 200°C for 2½ hours to represent the heat treated and hardened condition.
X-ray powder photographs were produced from these powders, and also from a pure tin standard, using a Phillips Debeye-Schierer camera with a Straumanis mounting. Filtered copper radiation was used.

3.9.2 Diffractometry

Quantitative X-ray diffraction was used to measure the volume fraction of SbSn present in rolled alloys, and also the lattice parameter of the tin rich solid solution as a function of antimony content. Solid rolled alloy specimens were used in this study since a range of deformations were required. These were electropolished using the methods described in section 3.6.1.

A standard Phillips diffractometer was used with filtered copper radiation. The angular scanning speed was $\frac{1}{8}$ degree 2θ per minute. A rotating stage was used to rotate the specimen about an axis perpendicular to its surface to remove the effects of texture in the plane of the sheet as this had proved troublesome. The effect of through thickness texture could not be removed in this way.

Lattice parameter measurements were also made on samples of a Sn/6% Sb alloy that had been rolled by 30% and 90%. Goniometer alignment and calibration adjustments were checked for drift and variation between runs. Since changes only occur in the 'a' direction the interplanar spacings of the tin(400) phases were measured since these are the highest order phases of the (h00) type that give a useful diffracted intensity.
The ratemeter time constant was kept at 1 second since larger values were found to shift the peak by significant amounts. This was satisfactory for high intensity peaks (large rolling deformation to develop texture), but on lower intensity peaks the rapid fluctuations made determination of the peak position difficult.

Later lattice parameter determinations were made by measuring the interplanar spacing of the Sn(620) planes since these lay at higher values of Sn 2θ and allowed greater measurement accuracy.

3.10 Differential Thermal Analysis

Differential thermal analysis was used to study the changes that occurred in pewter on heating from room temperature to just below the melting point, and hence the factors involved in the hardening process which accompanies this treatment.

Analysis was carried out between 0 and 225°C in a Du Pont thermal analyser fitted with a differential scanning calorimeter cell which enabled the rate of energy evolution or absorption to be determined at any temperature. The overall maximum sensitivity of the apparatus was 0.05 m cal/sec/mg of sample. Small samples of pewter (200 mg) were either cut or spark machined from the bulk, and compared with a standard of fully recrystallised commercial purity tin of the same weight. Heating or cooling rates were kept constant at 10°C/min for all the tests, and the specimen was surrounded by an atmosphere of oxygen free nitrogen at all times apart from loading and removal.
At the end of the test the cell was cooled from 225°C to room temperature in approximately 3 minutes using a liquid nitrogen cooling accessory, and the specimen removed for metallography.

3.11 Mechanical Testing

3.11.1 Variable Indentation Time Hardness Tests

Variable time hardness tests were carried out on samples of tin and rolled pewter containing 4% Sb, and 4% Sb + 2½% Cu, using an Akashi microhardness tester. This instrument is of the deadweight type, so that the time taken to attain full load is small compared to the indentation time. Three indentations were made for each test time, and the times were varied between 1 second and 180 seconds.

3.11.2 Tensile Creep Tests

Tensile creep tests were performed on pure tin, Sn/6% Sb and Sn/6% Sb/ 2½ alloys under constant load conditions at stresses between 5.9 and 45 MPa. Using a Tequipment lever arm creep tester. Creep extension was measured by a dial gauge attached to the lower gripping chuck, and measurements of elongation made to an accuracy of ±0.005 mm. Materials were tested after cold rolling (90% reduction) and after rolling followed by a heat treatment at 200°C for 1 hr followed by water quenching. The form of the specimen was the same as those used for tensile testing.
3.11.3 Variable strain Rate Tensile Tests

Differential or stepped tensile tests were carried out on an Instron T.T.D. testing machine at strain rates between $1.25 \times 10^{-3}$ and 1.25/min according to the method of Backofen, Turner and Avery. (85) Strain was measured directly from the specimen using a calibrated extensometer.

Tests were carried out by straining the specimen to 1% strain at the lower speed, and then instantaneously increasing the cross head speed by a factor of 2 or 2.5. This continued for a further 1% strain when the speed was returned to the lower setting. A new specimen was used for each test. The true flow stress was measured for both strain rates at 1% strain by a method of back extrapolation at the higher strain rate. The same stress levels were obtained after back extrapolation as were recorded for a new specimen strained to 1% at the higher strain rate.

![Typical Trace of a Specimen Strained at $\dot{\varepsilon}$](image)

Fig 10 $\sigma - \varepsilon$ diagram for a variable strain rate.
A new specimen was used for each test so that the rate change was made at the same total strain, and also to ensure small total tensile strains to avoid any chance of plastic instability.

3.11.4 Determination of Activation Energy for Deformation at low strain rates.

The activation energy for deformation at the two lowest strain rates (1.25 and 2.5 x 10^{-3}/min) was determined between 17°C and 70°C. For pure tin, tin/6% antimony alloy rolled to 90% reduction before testing, and the same material after solution treatment at 220°C.

The same testing arrangements were used as in section 3.11.3, but with the addition of an environmental chamber to surround the specimen and grips. This enabled the temperature to be controlled ± 1°C for temperatures above room temperature. Further tests were carried out on the rolled alloy at -10°C and -40°C using a liquid nitrogen supply activated by the chamber controller to maintain the set temperature ± 5°C.

The time between loading the specimen and testing was 20 minutes to allow specimen and grips to come to temperature.
4 Results

4.1 Hardness vs Deformation Curves for Pewter Alloys

Examination of the hardness/deformation curves for binary and ternary alloys shows that both exhibit two different kinds of behaviour. During the initial stages of deformation all the alloys tested showed an increase in hardness. This reached a maximum, in most cases, at 20% deformation. After the maximum the hardness fell continuously with deformation until at 90% reduction the hardness value was similar to, or less than, that of the cast material.

Figure 11 shows that a 6% antimony alloy had a cast hardness of 19 H.V. rising to a maximum of 22½ H.V. at 20% reduction. This fell to below the cast hardness (18 H.V.) at 90% reductions. Similar results were obtained for a 4%Sb alloy except that the cast and final hardness were lower, and the increase in hardness from the cast condition to the maximum was slightly less.

Ternary alloys containing 2-2½% copper in addition to antimony show an enhanced cast hardness, usually 5-7 H.V. in excess of the equivalent binary alloy. They display the same initial increase in hardness, which is at a maximum between 20 and 30% deformation, but then soften much more rapidly than the binary alloys, so that any hardness increase due to the addition of copper is lost on further rolling to 90% reduction.
FIG. 11
HARDNESS vs. DEFORMATION FOR Sn–Sb ALLOYS

VICKERS HARDNESS

94/6/0

96/4/0

PURE TIN

% REDUCTION

0 10 20 30 40 50 60 70 80 90
FIG. 12
HARDNESS vs. DEFORMATION FOR Sn–Sb–Cu ALLOYS
The hardness in this case is usually within $\frac{1}{2}$ H.V. of a binary alloy with the same antimony content. Hardness/deformation curves for ternary alloys are shown in Fig 12.

The tin/2% copper alloy prepared to investigate the effects of copper additions alone had an initial hardness of 13 H.V. This rose to 14 H.V. and remained practically constant up to 90% reduction (Fig 12).

The effect of rolling on the hardness of alloys based on conventional pewter compositions is summarised below.

<table>
<thead>
<tr>
<th>% Sb</th>
<th>% Cu</th>
<th>HV 0%</th>
<th>HV 20%</th>
<th>HV 90%</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>7.3</td>
<td>8.7</td>
<td>6.6</td>
</tr>
<tr>
<td>4</td>
<td>0</td>
<td>14.7</td>
<td>17.6</td>
<td>14.8</td>
</tr>
<tr>
<td>6</td>
<td>0</td>
<td>18.5</td>
<td>22.2</td>
<td>17.5</td>
</tr>
<tr>
<td>0</td>
<td>2</td>
<td>12.9</td>
<td>14.3</td>
<td>13.7</td>
</tr>
<tr>
<td>4</td>
<td>2$\frac{1}{2}$</td>
<td>20.3</td>
<td>22.5</td>
<td>16.3</td>
</tr>
<tr>
<td>6</td>
<td>2$\frac{1}{2}$</td>
<td>25.3</td>
<td>26.8</td>
<td>17.3</td>
</tr>
</tbody>
</table>

Table 17 Summary of Hardness Results

Brinell testing was also carried out under standardised conditions of hardness testing ($L/D^2 = 5$, time = 30 secs). Alloys tested contained 6% Sb and 6% Sb + 2$\frac{1}{2}$% Cu, and the results are shown below.
Reduction % | 6% Sb | 6% Sb + 2½% Cu
---|---|---
0 | 14.0 | 19.0
10 | 15.2 | 19.5
20 | 14.6 | 19.0
30 | 13.5 | 17.0
40 | 13.4 | 15.9
50 | 13.0 | 15.2
60 | 12.5 | 13.5
70 | 11.4 | 11.8
80 | 10.3 | 10.6

Table 18 Brinell Hardness of Pewter Alloys

4.1.1 Hardness/Deformation curves for Development Alloys

In addition to the work on pewter, other tin based alloys were prepared and tested to find whether improved properties could be obtained from different compositions. In particular an alloy was required that had a high hardness and a low softening rate with deformation. The composition of the alloys tested with the as cast and 90% deformed hardness values are shown below:

<table>
<thead>
<tr>
<th>Alloy Code</th>
<th>Sn</th>
<th>Ni</th>
<th>Bi</th>
<th>Sb</th>
<th>Zn</th>
<th>HV 90%</th>
<th>HV cast</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>99.7</td>
<td>0.3</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>10.0</td>
<td>10.7</td>
</tr>
<tr>
<td>B</td>
<td>98.7</td>
<td>0.3</td>
<td>1.0</td>
<td>-</td>
<td>-</td>
<td>15.3</td>
<td>14.8</td>
</tr>
<tr>
<td>C</td>
<td>96.7</td>
<td>0.3</td>
<td>1.0</td>
<td>2.0</td>
<td>-</td>
<td>16.9</td>
<td>17.7</td>
</tr>
<tr>
<td>D</td>
<td>97.2</td>
<td>0.3</td>
<td>1.0</td>
<td>1.0</td>
<td>0.5</td>
<td>16.2</td>
<td>21.3</td>
</tr>
</tbody>
</table>

Table 19 Composition of Alloys (wt %)
FIG. 13

HARDNESS vs. DEFORMATION FOR DEVELOPMENT ALLOYS

- A: Sn/0.3Ni
- B: Sn/0.3Ni/1Bi
- C: Sn/0.3Ni/1Bi/12Sb
- D: Sn/0.3Ni/1Bi/1Sb/0.5 Zn

VICKERS HARDNESS vs. % DEFORMATION
Rolling and hardness testing were carried out in an identical manner to that used for the conventional pewter alloys. Results are shown in figure 13.

Increasing amounts of alloying additions produced increasing cast hardnesses through the series of alloys A to D. This was not reflected in the 90% deformed condition as the higher strength alloys, particularly alloy D, tended to soften at a greater rate. These curves are in many ways similar to those obtained for pewter alloys, showing an increase in hardness at low deformation followed by softening on further rolling at a rate which is related to the initial hardness.

4.2 Heat Treatment of Rolled Pewter Alloys

Heat treatment of rolled pewter at temperature above 150°C is known to restore much of the hardness lost on rolling. This has been carried out in short term tests (up to 4 hrs) at 160°C, 180°C and 200°C on a series of ternary alloys. In addition long term tests were carried out at 200°C for periods of up to 240 hours. Results are shown in figs. 14 and 15. In all cases, excepting the 2% antimony alloy, a higher heat treatment temperature resulted in both an increased maximum hardness, and a shorter time to achieve a given hardness. The 2% Sb alloy did not harden significantly at any of the temperatures used.

None of the alloys tested quite regained their cast hardness, but they did approach very closely the hardness of alloys that had been subjected to a homogenising treatment of 72 hrs at 200°C after casting.
FIG 14

THE EFFECT OF HEAT TREATMENT TEMPERATURE AND TIME ON THE HARDNESS OF ROLLED PEBBER.

- - - - 200°C
- - - - 180°C
- - - - 160°C
<table>
<thead>
<tr>
<th>% Sb</th>
<th>% Cu</th>
<th>Cast Hardness</th>
<th>As cast + 72 hrs 200°C</th>
<th>As rolled + 3 hrs 200°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>6</td>
<td>2</td>
<td>22.5</td>
<td>19.5</td>
<td>19.5</td>
</tr>
<tr>
<td>4</td>
<td>2</td>
<td>19.1</td>
<td>17.5</td>
<td>17.3</td>
</tr>
<tr>
<td>2</td>
<td>2</td>
<td>15.6</td>
<td>13.1</td>
<td>13.0</td>
</tr>
</tbody>
</table>

Table 20  Hardness of cast and heat treated alloys

It was noted that several alloys heated at 160°C for 4 hours appeared to show slight softening. This behaviour was inconsistent with results at other temperatures. There was no indication of a fall in hardness in alloys heated to 200°C for either shorter or longer times. The slight dip in hardness for the 2%Sb,2%Cu alloy at 3 hours is not considered significant, and most probably arises from small local variations in hardness and hence the uncertainty of an 'average' result.

4.3 Metallography of Cast and Rolled Alloys

4.3.1 Tin-Antimony Alloys

Cast tin-antimony alloys are composed essentially of a cored tin rich solid solution with a grain size of approx. 2 mm. The grain boundaries are fairly well defined, but appear quite mobile. Plate 1 shows that in several instances they appear to have left the cored regions associated with their position at the time of solidification, and moved elsewhere under the influence of cooling stresses. A few small white particles of SbSn can be seen in the boundaries and at triple points.
During the early stages of deformation numerous deformation twins are formed, accompanied by the appearance of slip bands. Hardness testing also shows strain hardening of the matrix. Generally twinning only occurs on one set of twin planes in each grain (plate 2). However as deformation continues the twins may themselves become twinned, until at around 30% deformation multiple twinning and slip band formation renders the structure highly confused, and often it was not possible to identify the original grain boundaries. The number of white SbSn precipitates increased noticeably during this stage of the deformation process.

At rolling reductions greater than approx. 20% general room temperature recrystallisation commenced, although a small number of recrystallised grains may be formed at lower deformations (Plate 11). The start of general recrystallisation was found to correlate well with the onset of hardness reduction, both in the 6% antimony alloy, and in the 4% alloy where there was a long hardness maximum and softening did not start until 70% deformation. This was found to correspond to 50% recrystallisation. Delayed recrystallisation was only found in this alloy, all other compositions tested showed a more general tendency to recrystallise at deformations in excess of 20%, to give a very fine grain size and a further increase in the number of SbSn precipitates.

Under deformation conditions nucleation of the intermetallic phase SbSn appears to be restricted to grain boundaries, slip bands and twin boundaries, although the latter may be very numerous in any one grain.
Hence the number of possible sites for SbSn precipitation increases rapidly with deformation particularly after recrystallisation has commenced. Plate 3 shows a sample of a 6% antimony alloy rolled 90% which demonstrates the very fine recrystallised grain size along with the light etching SbSn precipitates in the grain boundaries. More detailed scanning electron micrographs showing precipitation in 4% Sb alloys can be seen in plates 7 to 9.

4.3.2 Tin-Antimony-Copper Alloys

Ternary tin-antimony copper alloys were prepared for examination in the same way as binary alloys. A variety of etches were used to show grain boundary delineation, but this proved difficult, and no one etch showed significantly improved performance. The situation was improved by the use of polarised light which gives enhanced grain contrast due to the optical anisotropy of the tin lattice. Since the SbSn phase does not exhibit this anisotropy it appears black under polarised light and hence there is little contrast between the SbSn particle and matrix grains so oriented as to be near to extinction. This problem was resolved by using Normarski differential interference contrast techniques which subjectively appeared to increase the contrast, although the image was still difficult to photograph.

Cast ternary alloys exhibited a varying grain size, although in all cases it was found to be finer than the corresponding tin-
antimony alloy. The first solid to be formed on cooling from the melt was the intermetallic Cu₆Sn₅ phase which appeared as long needles or rosettes. This was followed by the tin rich solid solution and more Cu₆Sn₅ as a dotted eutectic (Plate 4).

Small rolling reductions resulted in the fragmentation of the Cu₆Sn₅ needles, and voids were formed between the fracture faces as the constituent parts of the needle were milled apart, in the rolling direction. Less twinning was found in the ternary alloys than in the corresponding binary, and slip bands were more numerous. Small light etching particles were present in the grain boundaries. These were shown to be both SbSn precipitates and Cu₆Sn₅ eutectic by microprobe analysis, although the distinction was much less clear using optical microscopy alone due to the similarity in size and colour (plate 5).

Large total deformations of these alloys resulted in the complete break up of the Cu₆Sn₅ needles, and the voids formed by previous deformation were filled in by the flow of metal from the matrix phase. The original cast grain structure was replaced by a much finer structure of recrystallised grains which may have a mixed grain size and the quantity of SbSn increased noticeably. (plate 6)
4.3.3 Quantitative Metallography

Examination of rolled alloys showed that the recrystallised grain size decreased with increasing deformation, and results are shown below for 4% antimony alloys. Size determination was by reference to standard A.S.T.M. non-ferrous grain size charts, followed by conversion to mean grain diameter.

<table>
<thead>
<tr>
<th>% Reduction</th>
<th>50</th>
<th>60</th>
<th>70</th>
<th>80</th>
<th>90</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sn/4% Sb</td>
<td>30</td>
<td>25</td>
<td>13</td>
<td>17</td>
<td>10</td>
</tr>
<tr>
<td>Sn/4% Sb/2½% Cu</td>
<td>10</td>
<td>10</td>
<td>10</td>
<td>7</td>
<td>5</td>
</tr>
</tbody>
</table>

Table 21 Recrystallised grain size(μm) vs Rolling Reduction

These results are for average grain size in each specimen. The grain size was not completely uniform, and areas with a higher local population of SbSn precipitates had smaller grain sizes than average, and conversely areas depleted in SbSn had rather larger grain sizes.

To obtain a more uniform microstructure cast ingots were homogenised for 14 days at 220°C to remove visible coring. Rolling was carried out in the normal way, and the resulting strip examined for grain size. A more uniform distribution of SbSn was obtained with a much reduced grain size variation. The results for binary alloys at 90% reduction are shown below, including a 6% antimony alloy which had been coarsened after rolling by a heat treatment at 80°C for 10 days. In this conditions the grain boundaries had broken free of the precipitates and hence SbSn particles were found within the grains.
### Table 22 Recrystallised grain size vs composition

Determination of the area fraction of SbSn using the "Quantimet" was uninformative due to the poor resolution of the system and insufficient selectivity to discriminate between SbSn particles and light etching grains. Conventional point counting proved to be more suitable, and results for binary alloys are shown below.

<table>
<thead>
<tr>
<th>% Reduction</th>
<th>Vol fraction of SbSn</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>Very small</td>
</tr>
<tr>
<td>10</td>
<td>3.4 %</td>
</tr>
<tr>
<td>30</td>
<td>4.9 %</td>
</tr>
<tr>
<td>50</td>
<td>7.3 %</td>
</tr>
<tr>
<td>70</td>
<td>9.7 %</td>
</tr>
<tr>
<td>80</td>
<td>10.9 %</td>
</tr>
<tr>
<td>90</td>
<td>9.2 %</td>
</tr>
</tbody>
</table>

* SbSn precipitate size 4-7\( \mu \text{m} \).

### Table 23 Vol fraction of SbSn in 6% Sb alloys
The amount of SbSn was found to increase with deformation, particularly after the start of general recrystallisation, and reaches a maximum at about 70% reduction. After this stage in the rolling process the amount remains effectively constant if the rather high value for the 80% deformed specimen is disregarded. It is considered that the most likely source of error in this result arises from the uncertainty as whether a precipitate lies on the intersection of counting grid or slightly to one side; (see section 3.7). The error is too large to be due to counting statistics since 1500 points were counted. If the uncertainty in N counts is $\sqrt{N}$ this would correspond to a possible error of ± 0.3% in the volume fractions.

At 90% deformation the 4% Sb alloy contained 6.2% SbSn, and the 2% Sb alloy 0.7%. This gives approximate matrix antimony contents of 1.5%, 1% and 1.6% for the 6, 4 and 2% Sb alloys respectively.

Measurement was also carried out on the grain sizes of the development alloys containing nickel. Values of 25-30$\mu$m were obtained for the Sn/0.3% Ni and Sn/0.3%Ni/1%Bi alloys. This was complicated by the very poor grain boundary delineation in these alloys. It was not possible to measure the grain sizes in those alloys containing further additions of antimony and zinc since no grain contrast or grain boundary delineation could be observed after etching with a variety of etches.
4.3.4 Scanning Electron Microscopy

Scanning Electron Microscopy has been employed with electrolytically, and chemically etched specimens to examine structural features with high resolution. In alloys which have been lightly deformed particles of SbSn can be seen at the grain boundaries, within some grains, and on certain slip bands (plate 7 and 8). In addition plate 9 shows that the precipitates formed at high angle boundaries completely straddle the boundaries and intrude into the grains on both sides, whereas optical microscopy can only show the boundary precipitates, but gives no information as to whether the precipitate has grown into one grain or both.

Plate 10 shows the microstructure from a 90% deformed sample, and again the 2-3μm grain boundary precipitates of SbSn are evident. In addition a much finer dispersion of particles (0.1 - 0.3μm) can be seen at grain boundary positions and within the grains. Microprobe analysis does not reveal any elements apart from tin and antimony in these regions; and hence these particles appear to be SbSn. It must be stressed, however, that these regions of fine precipitation are not typical of the whole microstructure, and neither have they been found in other specimens in this condition or at lower percentage deformations.

Specimens that had been prepared by argon ion etching were also examined, but it was found that this preparation produced a fine dispersion of SbSn on the specimen surface which was not present before etching.
It is presumed that this was due to the high kinetic energy of the argon ions producing a large number of point defects in the surface regions of the specimen encouraging precipitation. Plate 11 shows a sample of 6% Sb pewter rolled by 10% and subsequently etched by this procedure.

4.3.5 Transmission Electron Microscopy

Thin foils

Transmission electron microscopy was carried out on pewter foils (4% Sb) to investigate the presence of any fine precipitates that might lead to precipitation hardening in lightly deformed alloys.

The preparation method described did not retain the original solution treated grain size (~30 μm dia x specimen thickness), and hence must have imparted an unknown degree of strain to the foil in the transparent region. Thin areas were formed at the ragged edges of the foil, but these were composed of extremely fine "mosaic blocks" (~500 Å) as shown in plate 12. No precipitates were seen in these areas, but the structure was so altered by the preparation procedure as to be meaningless.

Extraction Replicas

Extraction replicas were obtained from specimens of Sn/6%Sb by the methods described in section 3.6.2. Alloys were examined in the 20% deformed condition corresponding to maximum hardness, and in the 90% deformed condition which was the maximum deformation used in this investigation.
Plate 13 shows an area from the 20% deformed sample containing a number of precipitates that varied in size from 300Å to 2000Å. The precipitates contained an internal structure, and two appeared to contain twins. Although the size varied by a factor of 7 between the smallest and largest precipitates, the thickness is approximately uniform at an estimated 100–200 Å. This suggested a precipitate morphology that varied from roughly spherical at the smallest sizes to a flat disc at the largest. The diffraction pattern from these precipitates is also shown.

Plate 14 shows part of the extracted surface from the same specimen which had a completely different appearance to the structures previously observed. This had the form of 3 triangles joined together and was approximately 1.5μm in length with some internal structure and what appeared to be a twin. The single crystal diffraction pattern confirmed the existence of a twin, and showed the same reflections and d spacings as the ring pattern obtained from the small "precipitates". Analysis of the two diffraction patterns indicated a cubic F type lattice, and measurements of the spot positions are shown in table 24.
Table 24. Electron diffraction patterns from extraction replicas and data for Sb₂O₃

<table>
<thead>
<tr>
<th>From A.S.T.M. Index</th>
<th>Plate 13A</th>
<th>Plate 14A</th>
</tr>
</thead>
<tbody>
<tr>
<td>d I/I₀ h,k,l</td>
<td>d</td>
<td>d</td>
</tr>
<tr>
<td>6.44 12 111</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>3.218 100 222</td>
<td>3.16</td>
<td>3.263</td>
</tr>
<tr>
<td>2.788 40 400</td>
<td>-</td>
<td>2.822</td>
</tr>
<tr>
<td>2.559 11 331</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>2.276 2 422</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>2.45 3 511</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>1.972 42 440</td>
<td>1.939</td>
<td>2.006</td>
</tr>
<tr>
<td>1.887 2 531</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>1.681 35 622</td>
<td>1.654</td>
<td>1.699</td>
</tr>
<tr>
<td>1.611 11 444</td>
<td>1.588</td>
<td>-</td>
</tr>
</tbody>
</table>

Replicas obtained from the 90% deformed specimens (plates 15 and 16) showed grain boundary delineation in addition to a number of 500Å precipitates. Many of these precipitates were associated with grain or sub-grain boundaries but were much smaller than the 'normal' 2-3µm SbSn particles observed by optical microscopy. In addition fine precipitates could be seen in areas that corresponded to the grain interior, although not all the grain boundaries can be seen on the photographs, and hence it is still possible that these are grain boundary precipitates.
Due to their small size the precipitates diffracted weakly, and only gave rise to a few diffraction spots which did not allow indexing or the lattice to be identified with confidence. However the spot positions did appear to correspond to the expected positions for $\text{Sb}_2\text{O}_3$, but not for $\text{SnSb}$. Grain boundaries are not observed in the low deformation specimens, but in this case the grain size is very much larger and hence the chance of finding a well defined boundary showing contrast is correspondingly less.

4.4 X-ray Diffraction of Rolled and Heat Treated Alloys

4.4.1 Powder Diffraction Photographs

Powder diffraction photographs were obtained from filings from alloys rolled to 90% reductions, and also from similar filings heated to 200°C for 2½ hours in a vacuum. The most pronounced difference between the sets of diffraction patterns was the presence of lines due to the $\text{SbSn}$ phase in the deformed powders which were completely absent in the case of the heat treated powders. These showed only lines due to the tin rich solid solution, or the solid solution and $\text{Cu}_6\text{Sn}_5$ in the case of samples containing copper.

Values of $a = 5.83\AA$ were obtained for the matrix phase in all instances, with no change in parameter due to the change in antimony content of the solid solution. In spite of the most stringent precautions the degree of measurement accuracy was less than the expected change due to solid solution effects.
4.4.2 Diffractometry

Results were obtained for the variation in integrated intensity of the SbSn (200) and (220) peaks as a function of deformation with a range of binary and ternary alloys. These are shown in figs 16 to 19.

In all cases the intensity of the (200) reflections increased rapidly with deformation, whilst the intensity of the (220) reflections rose at a lower rate, and in some cases remained constant at higher deformations. If the precipitates were randomly oriented then the ratio of the (200) and (220) peak intensities would remain at a constant value and be independent of deformation. This is clearly not the case, and the results show that the precipitates texture as a result of rolling. The departure from random orientation is shown in figures 20 and 21. Whilst quantitative values for the volume fraction of SbSn cannot be obtained due to the non-random orientation, the results show strong qualitative indications that the amount of SbSn in the structure increases rapidly with deformation.

The lattice parameter and rhombohedral angle of the SbSn phase were determined, and gave values of \(a = 6.13\text{Å}\) and \(\alpha = 89.7\) for both binary and ternary alloys. This shows excellent agreement with the work of Hagg and Hybinette\(^{(19)}\) for SbSn at the tin rich boundary in tin-antimony alloys.
Fig. 16

- Sn/6% Sb/2% Cu
- Sn/6% Sb

Integrated intensity vs. % deformation.
FIG. 19

INTEGRATED INTENSITY SbSn (220)

- Sn/4% Sb/2% Cu
- Sn/4% Sb

% DEFORMATION

10 20 30 40 50 60 70 80 90 95
FIG. 20

% RELATIVE INTENSITY \( \left( \frac{I_{200}}{I_{100}} \right) \times 100\% \)

- \( \text{Sn/6\% Sb/2\% Cu} \)
- \( \text{Sn/6\% Sb} \)

RANDOM ORIENTATION

% DEFORMATION

0 10 20 30 40 50 60 70 80 90 95
FIG 21

% DEFORMATION

RANDOM ORIENTATION

Sn/4% Sb/2% Cu

Sn/4% Sb

% RELATIVE INTENSITY \((I_{200}/I_{100}) \times 100\%\)
Lattice parameter measurements were made in the 'a' direction for the tin rich solid solution in a 6% Sb alloy, but presented considerable difficulty, as the high order planes required to give an accurate parameter measurement also had a very low diffracted intensity. Initially the (400) interplaner spacing was determined in the 30% and 90% deformed condition: A value of \( a = 5.830 \text{Å} \) was recorded for both samples. This was an unexpected result and later determinations made use of the (620) peak. The following results were recorded for pure tin, 6% Sb alloys in the 90% deformed condition, and the same alloy after a solution treatment at 225°C for 2 hours. The temperature was accurately controlled at 25°C.

<table>
<thead>
<tr>
<th>Alloy</th>
<th>( 2\theta^\circ )</th>
<th>( d )</th>
<th>( a(\text{Å}) )</th>
<th>( a(\text{KX}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tin as rolled</td>
<td>113.425</td>
<td>0.92144</td>
<td>5.828</td>
<td>5.816</td>
</tr>
<tr>
<td>Sn/6% rolled 90%</td>
<td>113.331</td>
<td>0.92193</td>
<td>5.831</td>
<td>5.819</td>
</tr>
<tr>
<td>&quot; + 2 hours 225°C</td>
<td>113.213</td>
<td>0.92256</td>
<td>5.835</td>
<td>5.823</td>
</tr>
</tbody>
</table>

Table 25  X-ray diffraction results Sn(620) lines

The lattice parameter measured for tin in the 'a' direction was slightly smaller than that obtained by Lee and Raynor \(^3\) (5.820 KX). This may be due to small amounts of impurities in the present sample of 'pure' tin (Appendix I). Lattice parameter measurements of the rolled and solution treated alloys corresponded to matrix antimony contents of 0 and 1.8% respectively.
If however 0.004 KX units are added to all the present experimental results such that the lattice parameters for tin are in agreement with Lee and Raynor, then matrix antimony contents of 1.8% Sb are obtained for the rolled sheet, and 4.2% Sb. for the solution treated material.

4.5 Electron Probe Microanalysis

4.5.1 Bulk Specimens

Analysis of the matrix phase antimony content of pewter was carried out by both wavelength dispersive techniques and by using an energy dispersive analyser with the computerised deconvolution procedure previously described. Initial energy dispersive analyses were made on bulk specimens of homogenised SbSn to check the method for overall accuracy. The following results were obtained after suitable correction for absorption, fluorescence, atomic number etc, and showed excellent agreement with an independent chemical analysis of the specimen by Fry's Metals.

<table>
<thead>
<tr>
<th>E. D. S. Point Analysis (1)</th>
<th>44.2 wt% Sb</th>
</tr>
</thead>
<tbody>
<tr>
<td>&quot;</td>
<td>45.2 wt% Sb</td>
</tr>
<tr>
<td>By chemical analysis</td>
<td>45.4 wt% Sb</td>
</tr>
</tbody>
</table>

Samples of a 6% Sb alloy that had received a range of deformations between 0% and 90% were then analysed, and also standards of tin and antimony to determine the mean energy of the two pure components over the selected window width.
See p. 153-41 for explanation of high values.
Five point analyses were carried out on each specimen. The results obtained are shown below.

<table>
<thead>
<tr>
<th>% Deformation</th>
<th>% Sb (Min)</th>
<th>% Sb (Max)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1.5</td>
<td>7.3</td>
</tr>
<tr>
<td>30</td>
<td>2.6</td>
<td>4.8</td>
</tr>
<tr>
<td>50</td>
<td>4.2</td>
<td>7.0</td>
</tr>
<tr>
<td>70</td>
<td>1.6</td>
<td>9.0</td>
</tr>
<tr>
<td>90</td>
<td>5.0</td>
<td>8.3</td>
</tr>
</tbody>
</table>

Table 26. Deconvoluted matrix Sb results for Rolled Sn/6% Sb

Table 26 shows a wide variation in antimony content within each specimen and no consistent variation with deformation as would be expected. For reasons discussed in section 5 it was considered that the method was unable to give reliable results at low antimony concentrations.

Some further analyses were carried out using a wavelength dispersive spectrometer on alloys containing 2, 4 and 6% Sb in the 90% deformed conditions. The results are shown in table 27.

<table>
<thead>
<tr>
<th>Composition</th>
<th>Results % Sb</th>
<th>Mean value</th>
</tr>
</thead>
<tbody>
<tr>
<td>6% Sb</td>
<td>2.37, 2.00, 3.16, 2.78</td>
<td>2.58%</td>
</tr>
<tr>
<td>4% Sb</td>
<td>2.74, 3.12, 2.96, 2.56</td>
<td>2.85%</td>
</tr>
<tr>
<td>2% Sb</td>
<td>2.04, 2.35, 2.30, 2.1</td>
<td>2.20%</td>
</tr>
</tbody>
</table>

Table 27. W.D.S. Results for 90% deformed Pewter
Much better agreement was obtained between individual results in this instance, and also a very similar value was obtained for the matrix antimony content of all the three compositions. It should be noted that the result for the 2% Sb alloy was higher than the bulk composition.

4.5.2 Analysis of Extraction Replicas

The extraction replicas studied by T.E.M. were subsequently analysed with a J.E.O.L. JXA 50 A electron probe microanalyser in the transmitted electron mode to obtain the composition of the precipitates. A complete analysis was not possible, as elements of lower atomic number than sodium cannot be detected with the energy dispersive analyser. Use of the crystal spectrometer was unsuccessful due to rapid contamination of the specimen, this was in spite of the use of a liquid nitrogen cooled decontaminator. Also problems were encountered with excessive astigmatism such that structural features could no longer be seen. Both of these effects arose from the use of a much higher beam current. Results from the energy dispersive analysis system are shown below, but must be viewed with caution since the X-ray count rate was very low due to the small analysed volume, and the collected spectra required computer deconvolution (see 4.5.1).

No elements apart from tin and antimony were detected.
Table 28  E.P.M.A. analysis of Extraction Replicas

<table>
<thead>
<tr>
<th>Analysis No</th>
<th>% Sn</th>
<th>% Sb</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>77</td>
<td>23</td>
</tr>
<tr>
<td>2</td>
<td>82</td>
<td>18</td>
</tr>
<tr>
<td>3</td>
<td>96</td>
<td>4</td>
</tr>
<tr>
<td>4</td>
<td>75</td>
<td>25</td>
</tr>
</tbody>
</table>

4.6 Analysis of Etched pewter surfaces by Electron Spectroscopy

Electron spectroscopy of pewter surfaces was carried out at various stages in the preparation of extraction replicas to complement the results of electron probe micro analysis and gain a better understanding of the nature of the extracted material.

Specimens of rolled 6% Sb pewter were examined in the following conditions:-

1) As polished (with aluminia)

11) As (1) followed electrolytic etching - see section 3

111) As (11) followed by etching in Ferric Chloride

Analysis of the clean metal surface showed only antimony and tin to be present. Carbon was also detected, but this is always present as contamination. Analysis of the etched metal surfaces showed much reduced metal signals and emission lines corresponding to oxygen. No contaminants such as iron, Chlorine, aluminium etc were detected that might have arisen from the preparation.
Quantitative analysis results are shown below for tin and antimony in the three conditions examined.

<table>
<thead>
<tr>
<th>Condition</th>
<th>% Sn</th>
<th>% Sb</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polished Metal</td>
<td>94</td>
<td>6</td>
</tr>
<tr>
<td>Electrolytically etched</td>
<td>80.5</td>
<td>19.5</td>
</tr>
<tr>
<td>As above—oxide removed</td>
<td>87.5</td>
<td>12.5</td>
</tr>
<tr>
<td>Electrolytically etched + FeCl₃ etch</td>
<td>86.8</td>
<td>13.2</td>
</tr>
</tbody>
</table>

Table 29 E.S.C.A. Chemical Analysis of Pewter Surfaces

Further information was obtained by a study of the binding energy (B.E.) of the 4d electrons ejected from the tin and antimony atoms as shown below.

<table>
<thead>
<tr>
<th>Condition</th>
<th>Sn (B.E)</th>
<th>Shift</th>
<th>Sb(B.E)</th>
<th>Shift</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polished metal</td>
<td>485.4 ev</td>
<td>-</td>
<td>537.8 ev</td>
<td>-</td>
</tr>
<tr>
<td>Electrolytically Etched</td>
<td>487.4 &quot;</td>
<td>+ 2 ev</td>
<td>540.9 &quot;</td>
<td>+31 ev</td>
</tr>
<tr>
<td>&quot;</td>
<td>485.6 &quot;</td>
<td>+0.2 &quot;</td>
<td>538.4 &quot;</td>
<td>+0.6 &quot;</td>
</tr>
<tr>
<td>&quot; + 4 mins AIB*</td>
<td>487.5 &quot;</td>
<td>+2.1 &quot;</td>
<td>541.4 &quot;</td>
<td>+3.6 &quot;</td>
</tr>
<tr>
<td>&quot; + FeCl₃</td>
<td>487.5 &quot;</td>
<td>+2.1 &quot;</td>
<td>541.4 &quot;</td>
<td>+3.6 &quot;</td>
</tr>
</tbody>
</table>

* A.I.B. - Argon Ion Bombardment

Table 30 Sn 4d and Sb4d Binding Energies in Etched Pewter

As metals become oxydised so the binding energy moves to higher values and the chemical state of the surface can analysed in terms of the shift produced. The first row of results in table 30 correspond to the clean metal surface and act as datum points for subsequent chemical shift.
After electrolytic etching the tin peak has been shifted + 2 ev corresponding to an oxidised surface. The antimony peak has also been shifted to higher values (+ 3.1 ev) but is composed of a doublet one part of which corresponds to the oxidised state and the other to the metal. Careful examination of the tin peak shows that it is also skewed with a small metallic component in the oxide peak. The metallic ion ratios in the oxide are not the same as for the bulk metal, the oxide being enriched in antimony as shown in table 29. After 4 minutes argon ion bombardment the tin and antimony peaks have returned to their metallic positions due to the removal of the oxide. Typical oxide etching rates with this equipment are about 25Å/ minute suggesting a total oxide thickness of ~100Å after electrolytic etching. Since this is far greater than the escape depth of photoelectrons the presence of a metallic component in the oxide signal for electrolytically etched specimens indicates that the oxide is discontinuous or that metallic particles are dispersed within it. A total antimony content of 12½% was determined for the metal immediately beneath the oxide indicating that antimony has segregated to the metal/oxide interface.
The results for samples that had been etched in ferric chloride after electrolytic etching were similar to those for electrolytic etching alone, except that the antimony content was lower, and whilst the antimony signal showed small amounts of metal as well as oxide the tin peak showed only oxide.

4.7 Differential Thermal Analysis

Results of thermal analysis are shown in figs 23 and 24 for binary and ternary pewter alloys after 90% rolling reduction. The general shape of this family of curves is shown below, and may be conveniently divided into 3 regions.

![Schematic D.T.A. Trace for Pewter](image)

Fig 22 Schematic D.T.A. Trace for Pewter

In region I the trace is substantially level using spark machined specimens. Some earlier specimens that had been prepared by sawing and grinding on silicon carbide discs gave a rising trace in this region. Hence it must be inferred that exothermic indications at this stage are an artifact from the preparation method.
The second region between 110°C and 200°C is characterised by an endotherm which can be related to the resolution of SbSn with a maximum rate at 170°C. The resolution start temperature of 100-110°C indicates an equilibrium matrix antimony content of about 1.3% Sb using Eyre's data for the α/α+β phase boundary, although there may be some overheating before resolution at the heating rates employed. This would lead to an overestimate of the antimony concentration.

The third part of the curve is a relatively flat region that continues up to the melting point indicating that resolution is virtually complete. Although the resolution endotherm has been passed the trace does not return to the baseline, however, but lies some way below it. This is frequently found in thermal analysis and is usually attributed to a change in specific heat; in this case between matrix and SbSn, and matrix only, with a higher antimony concentration and a lower specific heat.

Tests have also been carried out where the heating has been interrupted at 155°C and the specimen held at that temperature for half an hour. Cooling the specimen rapidly to 60°C followed by reheating at 10°C/min resulted in a flat trace up to a temperature of 160°C with a fall off at higher temperatures (Fig 25). The isothermal treatment at 155°C will result in a partial resolution of SbSn to give a matrix antimony content of 2.3% at equilibrium.
FIG. 23

D.T.A. TRACES FOR ALLOYS ROLLED 90%
FIG. 25

D.T.A. TRACE FOR Sn/6% Sb ALLOY ROLLED 90% AND HELD AT 155°C

Pen reset and specimen reheated after isothermal hold at 155°C

Hold at 155°C for 35 mins

0.05 m.cal/sec

20 40 60 80 100 120 140 160 180 200 220
TEMPERATURE °C
Reheating results in a level trace until the new phase boundary is crossed when the remaining SbSn, at equilibrium with a matrix of higher antimony content, begins to re-dissolve. The observed fall off at higher temperatures is considered to be a combination of the resolution endotherm from the remaining SbSn precipitates and a further change in specific heat.

Cooling the specimens from the solution treatment temperature (>220°C) results in a level trace parallel to the baseline indicating that no re-precipitation has occurred on cooling. Similarly reheating the specimen again results in an another straight line parallel to the baseline.

4.7.1 Metallography Of D.T.A. Specimens

The structural changes accompanying the heating of rolled pewter at 10°C/minute have been studied by metallography, and are shown in plates 17 to 19.

The structure obtained at 110°C is very similar to that at room temperature except that limited grain growth has occurred in some areas, principally those areas where the amount of SbSn precipitation is lower than average (plate 17). This temperature corresponds to the end of region I in the DTA curve which is flat and parallel to the baseline.

Further heating to 170°C, which is the minimum point of the SbSn resolution endotherm, results in a partial resolution of the precipitates. Plate 18 is a micrograph obtained by rapidly cooling from this temperature and shows a decreased density of precipitation as would be expected.
In addition the grain size has increased.

Complete resolution is obtained at temperatures in excess of 200°C for specimens containing 4% Sb. Plate 19 shows the structure after heating to 225°C. All the precipitates on the original grain boundaries have dissolved and the grain size is much increased (~0.3 mm). Some precipitates can still be seen in the new grain boundaries, but it is considered that these were formed after cooling to room temperature, and are similar to those observed in cast ingots. In addition the regions of coring associated with the dissolved precipitates can be seen within the grains.

4.8 Mechanical Testing

4.8.1 Variable Indentation Time Hardness Tests

Vickers microhardness tests have been carried out on a series of alloys for indentation times between 2 and 300 seconds. Results were obtained for the stress exponent (n) using the equation derived by Murty (49).

\[
\log d = A_2 - \left(\frac{1}{2n - 1}\right) \frac{Q}{RT} + \left(\frac{1}{2n - 1}\right) \log (t + a)
\]

Plots of log indentation time (t) against log indentation diameter (d) have a slope of \(\frac{1}{2n - 1}\) at longer indentation times (t >> a) and are shown in Fig 26. Values of n determined from these plots are shown in table 31.
Table 31

<table>
<thead>
<tr>
<th>Material</th>
<th>n</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure tin (rolled 90%)</td>
<td>7.5</td>
</tr>
<tr>
<td>Sn/4% Sb ( &quot; &quot; )</td>
<td>5.8</td>
</tr>
<tr>
<td>Sn/4% Sb/2½% Cu ( &quot; &quot; )</td>
<td>5.8</td>
</tr>
<tr>
<td>Sn/4% Sb (rolled + 1 hour at 200°C)</td>
<td>15</td>
</tr>
<tr>
<td>Sn/4% Sb/2½% Cu (rolled &quot; &quot; &quot; &quot; )</td>
<td>11</td>
</tr>
</tbody>
</table>

Table 31

Stress Exponents obtained from Hardness Tests

4.8.2 Tensile Creep Tests

Tensile creep tests were carried out at stress between 5 and 45 MPa. using pure tin, and 6% Sb binary and ternary pewter alloys. These were tested both in the 90% deformed condition and also after heat treatment of 1 hour at 200°C. The steady state creep rates were determined at a constant room temperature of 25°C, and plots obtained for logσ against log ɛ. These gave straight lines of slope n and are shown in figs 27 and 28. The values of the stress exponent (n) were determined by at least mean squares analysis of the data, and are shown below.

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure Tin (rolled 90%)</td>
<td>6.1</td>
</tr>
<tr>
<td>&quot; &quot; (rolled 90% + 1 hour at 200°C)</td>
<td>6.6</td>
</tr>
<tr>
<td>Sn/6% Sb (rolled 90%)</td>
<td>4.1</td>
</tr>
<tr>
<td>&quot; &quot; (rolled 90% + 1 hour at 200°C)</td>
<td>16.2</td>
</tr>
<tr>
<td>Sn/6% Sb/2½% Cu (rolled 90%)</td>
<td>4.8</td>
</tr>
<tr>
<td>&quot; &quot; &quot; (rolled 90% + 1 hour at 200°C)</td>
<td>11.1</td>
</tr>
</tbody>
</table>

Table 32 Stress Exponents obtained from Creep tests
FIG 2.7
TENSILE CREEP TEST RESULTS FOR TIN AND ROLLED PEWTER

1. Tin rolled 90% + 1 hr. @ 200°C
2. Tin rolled 90%
3. Sn/6%Sb/2½%Cu rolled 90%
4. Sn/6%Sb rolled 90%
FIG 28
TENSILE CREEP RESULTS FOR HEAT TREATED PEWTER

5 Sn/6% Sb — rolled+1 hour @ 200°C
6 Sn/6% Sb/2½%Cu

\[ \dot{\varepsilon} / \text{hour} \]

\[ \dot{\varepsilon} \quad 10^{-2} \quad 10^{-1} \]

\[ \text{STRESS (MPa)} \quad 1 \quad 10 \quad 100 \]
4.8.3 Variable Strain Rate Tensile Tests

4.8.3.1 The strain rate dependance of flow stress in Pewter Alloys.

Tests were carried out at constant (room) temperature by the methods described in section 3.11.3 at strain rates between $1.25 \times 10^{-3}$ and 1.25/minute.

Materials tested in the 90% deformed condition were pure tin, binary pewters containing 2, 4, and 6% antimony, and a 6% Sb, 2% Cu ternary pewter. In addition the 6% Sb binary and ternary pewters were tested after a high temperature heat treatment at 200°C, and the 6% Sb binary alloy after a grain coarsening treatment of 10 days at 120°C. The logarithmic plots of flow stress against strain rate are shown in figures 29 to 31.

Figure 29 shows that for a 90% deformed 6% antimony binary alloy the plot of the log true flow stress against log strain rate $(\log \sigma / \log \dot{\varepsilon})$ is a straight line of slope 0.25 up to a limiting value $(\dot{\varepsilon} = 5 \times 10^{-2}/\text{minute})$. At higher strain rates the line becomes curved, and tends towards a slope of 0.1. The slope of the line is the strain rate sensitivity (S.R.S), and a change in this parameter indicates a change in deformation mode as discussed in section 5.3. Briefly a low value of the S.R.S. indicates deformation by conventional plasticity, whilst the higher values obtained at low strain rates indicate that a contribution to the overall deformation strain is provided by grain boundary sliding.
Figure 29 also shows plots for the same material after solution treatment, and also after a grain coarsening heat treatment of 10 days at 80°C. This was below the resolution temperature of the precipitates but allowed the grain size to be coarsened to 90 μm. The solution treated specimens gave a straight line on the log σ/\log \dot{\varepsilon} plot with a very low value of the S.R.S. At low strain rates this material had a much higher flow stress than the rolled sheet, but at high strain rates the situation was reversed, so that the 'soft' rolled pewter was stronger than the 'hard' heat treated material. Specimens that had been subject to the coarsening treatment showed intermediate properties with a straight line plot of log σ/\log \dot{\varepsilon} of low SRS.

Figure 30 shows the same information for a 6% Sb 2½% Cu ternary alloy. The plot for the 90% deformed specimens was identical to that for the binary alloy, whilst the material heat treated at 200°C for 1 hour showed a similar line to the solution treated binary alloy, except that it was displaced to higher flow stresses. This is consistent with the known higher hardness of heat treated ternary alloys, when compared to binary alloys of the same antimony content.

Also shown is the log σ/\log \dot{\varepsilon} plot for pure tin. This was a straight line of SRS 0.1 but with a much lower range of flow stresses than the pewter alloys.
Fig. 29

Stress vs. strain rate for homogenised 6% Sb pewter

As rolled (90%)
 Rolled + 10 days at 80°C
 Rolled + 1 hour at 225°C
FIG. 30
STRESS vs. STRAIN RATE
FOR 6% Sb, 2½% Cu PEWTER

As rolled (90%)
FIG 31

STRESS vs. STRAIN RATE FOR TIN AND HOMOGENISED Sn–Sb ALLOYS
Similar data is shown for 90% deformed alloys containing 2, 4 and 6% antimony in figure 31. These alloys form a series with increasing volume fractions of SbSn as the antimony content is increased, and also decreasing grain size (70 μm, 4 μm and 2 μm) respectively. All the plots show a similar trend of a high SRS up to a limiting value of 2.5 x 10⁻²/min followed by a decreasing SRS at higher strain rates, but are displaced on the stress axis to higher flow stresses at higher antimony content. Metallographic examination of specimens revealed no evidence of grain growth during the test.

4.8.3.2 Ductility of Pewter in Tensile Tests

Specimens of 6% Sb pewter were tested to failure in tension over a range of strain rates and temperatures. Results are presented in figure 32.

At room temperature the rolled specimens showed a sudden transition from high ductility (>150%) with multiple necking, to lower ductility behaviour (60%) as the strain rate was increased. This was associated with the reduction of the strain rate sensitivity factor (m). Reducing the temperature to -10°C produced a curve of very similar shape, except that the ductilities were much reduced (75% to 35%). This did not, however, alter the transition strain rate between high and low ductility behaviour, which occurred in the range 1.25 x 10⁻² to 1.25 x 10⁻¹/minute. Further reduction of the temperature to -40°C produced a flat straight line plot at 32.5% elongation.
Fig. 32: Ductility of Rolled 5% Sb Pewter vs. Strain Rate and Temperature.

1. Rolled 90%, tested at 20°C.
2. " " −10°C
3. " " −40°C
4. " +10 days @ 80°C, tested at 20°C

% Ductility

10^1

10^2

10^3

ε/Min
The wide variation of ductility in rolled pewter may be contrasted with the almost uniform ductility of the same material after grain coarsening which ranged from 62% to 46% over four orders of magnitude of strain rate. This behaviour can be related to the almost constant value for the SRS for the material in this condition.

The deformation process was studied further by polishing the specimen in a transverse direction with 1μm diamond compound. This left distinct scratches on the specimen surface. After 30% deformation at room temperature and a strain rate of $1.25 \times 10^{-3}$ /min the specimen was removed from the Instron and examined in the S.E.M. It was found that the marks were offset at the grain boundaries and showed grain rotation. Also grains had intruded and extruded from the surface (plate 20).

A specimen tested to failure under identical conditions was sectioned in the longitudinal direction and examined for cavitation. There was no evidence of any porosity adjacent to the fracture surface or elsewhere in the specimen (plate 21). By contrast a single specimen of rolled Sn/6% Sb/2% Cu alloy was tested under the same conditions and sectioned. Extensive cavitation was found close to the fracture surface and over a considerable amount of the necked region, although the failure strain was similar in both cases.
Close examination of the cavitation showed that it was associated with the interface between the matrix and Cu₆Sn₅ particles. (plate 22)

4.8.3.3 The strain rate dependance of flow stress in Development Alloys.

Variable strain rate tensile tests were carried out on alloys A, B and C after 90% rolling reduction, to understand more fully the nature of the hardness reduction. It was not possible to test alloy D in this way due to persistent porosity in the ingot which led to defects in the rolled strip. Results of these tests are shown in figure 33 along with transposed results for Sn/6%Sb/2½%Cu for comparison.

It can be seen that the traces for alloys A and B have a similar form with m = 0.17 except that alloy B with 1% Bismuth is displaced to higher stresses. The ratio of the flow stresses at any particular strain rate are approximately the same as the ratio of the hardnesses. Alloy C shows a different behaviour with a higher strain rate sensitivity. Although it has a higher hardness than alloy B due to the addition of 2% antimony its properties are inferior at low strain rates, and superior at high strain rate. On balance this gives a higher hardness in a Vickers test which is a combination of high and low strain rate testing.
FIG 33
STRESS vs. STRAIN RATE FOR DEVELOPMENT ALLOYS

A Sn-0.3% Ni
B Sn-0.3% Ni-1% Bi
C Sn-0.3% Ni-1% Bi-2% Sb

LOG_{10} STRESS (MPa)

ε / MIN

10^{-3} 10^{-2} 10^{-1} 1
The traces for alloy C and the 6% Sb, 2\(\frac{1}{4}\)% Cu pewter are very similar in shape, but the development alloy shows improved properties over the entire strain rate range investigated.

4.9 Electron Microscopy of Fracture Surfaces

Specimens of 6% antimony pewter rolled to 90% reduction have been tested to failure in tension at temperatures of 20°C, -10°C and -40°C at strain rates between 1.25 \(\times\) 10\(^{-3}\) and 12.5 per minute as described in section 3.11.3. Scanning electron micrographs of the fracture surfaces were obtained and show a number of trends as the strain rate was increased or the temperature was decreased (plates 23 to 41).

4.9.1 Room Temperature Tests

At room temperature and slow strain rates large ductilities were found (150%) accompanied by a large reduction in area to give a knife edge fracture. Small deep voids (\(~15\,\mu\text{m}\)) are present along the fracture edge. Examination of the void interiors showed a rough intercrystalline appearance (plate 26).

As the strain rate was increased to 1.25 \(\times\) 10\(^{-2}\) the fracture edge became slightly broader and with more visible voids (plate 24). Also, fine 45° shear bands could be seen on the side of the specimen. At the highest strain rate (12.5/min) the type of failure changed to a blunt ductile fracture showing a typical "dimpled" surface indicative of microvoid coalescence, as did all the specimens tested at this \(\varepsilon\).
The dimple size was approximately $4 \mu m$ (plates 27 and 27a). Large voids were still present in the fracture surface, but at this high strain rate they were smooth sided in contrast to the intergranular appearance of those observed at low strain rates.

4.9.2 Tests at $-10^\circ C$

Low temperature tests were carried out over a smaller range of strain rates than at room temperature since the transition from a knife edge to a blunt ductile failure occurs at much lower testing speeds. At $1.25 \times 10^{-3}/\text{min}$ the fracture appearance was very similar to that obtained at room temperature, except that shear bands could be seen on the sides of the specimen and the overall ductility was lower. (Plate 28)

Increasing the strain rate to $1.25 \times 10^{-2}/\text{min}$ gave a more blunt ductile fracture, with many small voids which again showed intergranular decohesion (plate 29). At $5 \times 10^{-2}/\text{min}$ the fracture was similar, except that the void interiors were smoother.

4.9.3 Tests at $-40^\circ C$

All the specimens tested at $-40^\circ C$ were characterised by very blunt fractures showing a ductile failure by microvoid coalescence and $45^\circ$ shear bands on the specimen surfaces. (Plates 31 - 33) Again many voids could be seen on the fracture surfaces, but their internal appearance was dependant on strain rate.
All were very granular (plate 34) but at the highest strain rate used \(5 \times 10^{-2}/\text{min}\) the interior showed ductile dimples (plate 35) suggesting tearing.

4.9.4 Coarsened structures tested at room temperature

Tensile tests were carried out on samples of rolled 6% Sb pewter that had their microstructures coarsened by a heat treatment at 80°C for 10 days. In this condition their strain rate sensitivity was reduced to one half of that of the as rolled specimens.

At \(1.25 \times 10^{-3}/\text{minute}\) the fracture was similar to that found in the as rolled alloys, although the ductility was much less (plate 36). Coarse slip bands could be seen on the sides of the specimen, they had an approximate spacing of 25 \(\mu\)m, and were much more evident than those observed in the rolled alloy at high strain rates (12.5/min).

Coarsened specimens tested at 12.5/min showed a fairly blunt ductile failure with many smooth voids. The size of the ductile "dimples" was larger than those found in the as rolled specimens due to the increased grain size (plates 37 and 38).

4.9.5 Tests on Solution Treated Specimens

Solution treated specimens of 6% Sb pewter were tested to failure at room temperature and a strain rate of \(1.25 \times 10^{-3}/\text{min}\). A pointed fracture was obtained at 20% elongation with no evidence of void formation. The fracture does not show the ductile appearance found in rolled or
coarsed specimens, and appears to be transgranular and to have formed by macroscopic slip in the coarse grains rather than by a ductile necking process (plates 39 to 41). This is discussed in section 5.4.

4.10 Determination of the Activation energy for creep

The activation energy for the deformation of rolled 6% antimony pewter at strain rates of 1.25 and \(2.5 \times 10^{-3}\)/minute has been determined over a temperature range of \(+70\degree C\) to \(-12\degree C\) (0.68 - 0.52 Tm) by the methods described in section 3.11.4. In addition similar determinations have been made for solution treated pewter and pure tin at the same strain rate over a more restricted range of temperatures.

The steady state creep behaviour of metals in the range of temperatures and strain rates investigated has frequently been described by equation 1.

\[
\dot{\varepsilon} = A \sigma^n e^{\frac{-Q}{RT}} \quad \text{(1)}
\]

Taking natural logarithms of both sides and rearranging gives:

\[
n \ln \sigma = \ln \dot{\varepsilon} - \ln A + \frac{Q}{RT} \quad \text{(2)}
\]

Since \(A\) and \(\dot{\varepsilon}\) are constant for any one series of tests:

\[
n \ln \sigma \propto \frac{Q}{RT} \quad \text{(3)}
\]

or

\[
\ln \sigma \propto \frac{Q}{nRT} \quad \text{(4)}
\]
Hence a plot of \( \ln \sigma \) against \( \frac{1}{T} \) should be a straight line of slope \( \frac{Q}{nR} \). These plots are shown in figure 34. Tensile creep tests are normally carried out under conditions of constant load or constant stress. In this case tests were carried out at constant strain rate so that the stress exponent \( n \) is not immediately available, but is related to the strain rate sensitivity factor \( m \) since \( \dot{\varepsilon} \propto \sigma^n \) and \( \sigma \propto \dot{\varepsilon}^m \) at constant temperature. Hence \( n = \frac{1}{m} \) for steady state creep. Table 33 below shows the values of \( Q \) obtained.

<table>
<thead>
<tr>
<th>Material</th>
<th>( Q/nR )</th>
<th>( n )</th>
<th>( Q ) Kcal/mole</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure tin (a)</td>
<td>966</td>
<td>11.13</td>
<td>21.3</td>
</tr>
<tr>
<td>&quot; &quot; (b)</td>
<td>1013</td>
<td>&quot;</td>
<td>22.3</td>
</tr>
<tr>
<td>Sn/6% Sb Rolled 90% (a)</td>
<td>1735</td>
<td>4.63</td>
<td>16.0</td>
</tr>
<tr>
<td>&quot; &quot; &quot; &quot; &quot; (b)</td>
<td>1779</td>
<td>&quot;</td>
<td>16.3</td>
</tr>
<tr>
<td>As above + 1 hr 225°C (a)</td>
<td>1018</td>
<td>18.3</td>
<td>36.9</td>
</tr>
<tr>
<td>&quot; &quot; &quot; &quot; &quot; &quot; (b)</td>
<td>1008</td>
<td>&quot;</td>
<td>36.5</td>
</tr>
</tbody>
</table>

(a) \( \dot{\varepsilon} = 1.25 \times 10^{-3} / \text{min} \) \hspace{1cm} (b) \( \dot{\varepsilon} = 2.5 \times 10^{-3} / \text{min} \)

Table 33 Activation Energy for the creep of tin and Pewter

The value of \( Q \approx 22 \) Kcal/mole for pure tin shows excellent agreement with values for the literature of 21-26 Kcal/mole for tin self diffusion\(^{(32)}\) and creep\(^{(56)}\). The values of \( n \) used to calculate \( Q \) are the average values obtained between the two strain rates over the range of temperatures investigated.
FIG. 34
Log_10 \sigma vs. 1/T plots for Tin and Sn/6%Sb.

\dot{\varepsilon}_1 = 1.25 \times 10^{-3} / \text{min.}
\dot{\varepsilon}_2 = 2.5 \times 10^{-3} / \text{min.}

Sn/6%Sb rolled 90% + 1 hour @ 225°C

Sn / 6% Sb rolled 90%
Determination of the activation energy for rolled pewter at low temperatures ($T < 0.5 \, T_m$) have not been made since this is outside the normal temperature range where creep process predominate at low strain rates. Any values obtained would have doubtful physical significance as they would include excess contributions from strain hardening and the effects of cold work.
5. Discussion

In the following chapter much reference will be made to the mechanical properties of tin based alloys measured at room temperature (20°C). It must be born in mind at all times that this corresponds to a homologous temperature of approximately 0.6 Tm which is well within the temperature range where time dependant creep processes operate. Thus values obtained during mechanical testing will be highly dependant on the testing conditions, and care is necessary when comparing the results of this investigation with those found in the literature, and drawing comparisons between different types of test in the same investigation.

5.1 The Hardness of Cast Pewter

The hardnesses of cast pewter used in this work is summarised in table 20, which shows that for tin-antimony alloys the increase in hardness on alloying is directly proportional to the solute concentration in agreement with the results of Hanson and Pell-Walpole\(^{(46)}\). Also the Brinell Hardnesses shown in Table 18 are in good agreement with the collected data produced by T.R.I.\(^{(38)}\) for standardised testing conditions, which again show a linear dependance of hardness on solute content up to 10% Sb.
At antimony concentrations greater than 10% the T.R.I data shows a much reduced rate of strengthening, which corresponds to the first appearance of SbSn cuboids formed on cooling from the liquid. Hence the composition of the primary supersaturated solid solution is less than the overall composition of the alloy due to the separation of a second phase.

The hardening effects of small copper additions to tin are less easy to explain since the solid solubility at the eutectic temperature is 0.0056%\(^{(27)}\), and by analogy with other systems this will decrease with temperature. The hardness data reproduced in table 5, shows that 1% of copper nearly doubles the hardness of tin, but further additions result in only a small increase. Unfortunately data for additions of less than 1% Cu are not available. Whilst the increase in hardness at higher copper contents must be presumed to be due to dispersion hardening from the increasing volume fraction of Cu\(_6\)Sn\(_5\) the hardening effect of the first 1% addition appears disproportionately large considering the very small solid solubility. This may be explained to a large extent by considering the interstitial nature of a copper atom when dissolved in the tin lattice as shown by the diffusion results of Dyson and others\(^{(32,35-37)}\) (section 2.2).
Drawing an analogy with the effects of solute additions to iron, it is well known that interstitial elements such as hydrogen, carbon, nitrogen etc., have a very strong influence on the hardness of ferrite even though their solubility is extremely limited. By comparison substitutional solutes such as Ni, Cr, Mn etc show a much smaller effect. Similarly small additions of copper in tin might be expected to show a relatively large change in hardness which is not shown to the same extent by antimony additions.

Figures 11 and 12 show that in cast alloys the addition of 2½% Cu results in a 6 HV increase in hardness irrespective of the antimony content, and hence the actions of the substitutional and interstitial solutes are independent and cumulative. These results are contrary to the hardness trends shown in table 5, collected from the literature, where smaller hardness increases are obtained by adding small amounts of copper to tin-antimony alloys than is the case for copper additions to tin alone. This discrepancy can be explained by considering the duration of the hardness test. The results from this investigation are Vickers Hardness numbers with an indentation duration of approximately 5 seconds, whereas the values in the literature were obtained by Brinell testing with an indentation duration of 30 seconds.
Hence in the Brinell test a much larger proportion of the test strain is due to time dependent creep affects. From this it must be inferred, that at stresses sufficient to cause gross yielding from the application of the indenting load, the relative creep rates of tin-antimony-copper alloys are greater than those for tin-copper alloys. Support for this view will be found in later sections.

5.2 The Effects of Progressive Deformation on Pewter Alloys

Metallographic examination and hardness tests at varying amounts of rolling reduction show that there are two distinct stages in the response of pewter to rolling. In the first stages of rolling, between the cast condition and the hardness maximum, at approximately 20% deformation, the original grains are deformed to give a strain hardened structure containing many deformation twins and slip bands. The coring produced during solidification is retained, and in addition some SbSn precipitation occurs on the original grain boundaries. A small number of recrystallised grains may be formed at this time, but their number does not become significant until the later stages of deformation. Hardness tests show a universal hardening response to deformation in these early stages for all pewter compositions, and for pure tin, which is consistent with strain hardening.
In the binary pewter alloys the maximum increase in hardness is related to the antimony content such that the 6% Sb alloy was hardened by 4HV, the 4% Sb alloy by 3HV, and pure tin by 1,5 HV (fig 11). With alloys containing copper the hardness increase is approximately constant at $1\frac{1}{2} - 2$ HV, irrespective of antimony content (fig 12). Thus increasing amounts of antimony are found to increase the work hardening rate of binary pewter alloys, whilst in ternary alloys of the same antimony content the rate is reduced somewhat. These results are in general agreement with those of Leyman (45), except for his 7% Sb alloy which shows a lower amount of hardening. This is, however, beyond the range of compositions studied in this investigation. Quantitative microscopy reveals that significant amounts of SbSn are precipitated during the very early stages of deformation (up to 10% reduction) on twin boundaries, and particularly on active slip bands and grain boundaries (plate 2), whilst in the cast condition the grain boundaries contain only a small number of precipitates (plate 1). Although twin boundaries and slip bands provide new sites for easy nucleation, this does not explain why there are so few precipitates on pre-existing boundaries before deformation.
It must be presumed that an enhanced diffusion rate provided by the increased dislocation density is necessary to create a sufficient flux of antimony atoms to the grain boundaries to account for the density of precipitates. As rolling proceeds a second stage is reached at which general room temperature recrystallisation commences. This is associated with the onset of softening. The rate of softening and the final hardness achieved after 90% deformation is dependent on the alloy composition. Results for pure tin and Sn-Sb alloys show that the final deformed hardness is very similar to the cast hardness, with only a 1 HV drop in the case of a tin-6% Sb alloy. The magnitude of the hardness drop from the maximum at 20% deformation to the 90% deformed value is equivalent to the removal of the effects of strain hardening. However the microstructure in the two conditions is very different and it will be shown later that the decrease in hardness cannot be explained on the basis of recrystallisation alone since the rolled alloy has experienced an additional loss of solid solution strengthening. Also it will be shown (section 5.4.1.) that the similarity between cast and rolled hardness for binary alloys is largely coincidental and due to the testing conditions chosen. If a Brinell test is used rather than a Vickers test, a 6% Sb alloy can be shown to be softened by rolling. (table 18).
Ternary alloys exhibit a much larger reduction in hardness, which is also composition dependant, with higher antimony additions leading to a greater degree of softening. Comparing figures 11 and 12 it can be seen that although alloys containing copper in addition to tin and antimony have a higher initial hardness, the rate of softening is greater, and at 90% reduction ternary alloys have a very similar hardness to binary alloys of the same antimony content.

Since ternary alloys soften to below the cast hardness explanations of the softening based on recrystallisation alone are untenable. Equally the loss of solid solution strengthening cannot be responsible in isolation since figure 11 shows that 90% deformed alloys of high antimony content are still harder than low antimony alloys even though the matrix antimony contents are similar. Clearly a description of the softening process needs to take account of the more complex interactions of matrix solute content, precipitate size and volume fraction and grain size, and much of the experimental work has been directed towards quantifying these variables. The implications of the interactions on the flow stress will be considered in section 5.3.1.
5.2.1 Quantitative Description and Analysis of Microstructure.

Measurements of the volume fraction of SbSn present in rolled alloys have been made by several techniques. X-ray powder diffraction photographs have shown the presence of SbSn in deformed material, and its absence after solution treatment. A quantitative extension of this technique using diffractometry in conjunction with rolled and cast specimens was used to provide values for the volume fraction of precipitate. However it was found that the precipitate textured strongly as a result of rolling and reliable quantitative data could not be obtained due to the departure from random orientation of the SbSn precipitates (fig 20 and 21). There was however a general trend of increasing amounts of SbSn being associated with higher deformations (figs 16 to 19). These observations were further reinforced by measurements obtained from other techniques.

The alternative x-ray technique of measuring the lattice parameter of the matrix phase as a function of deformation, and hence the residual matrix antimony content has also been employed. The change in parameter as a function of antimony content has been studied by Lee and Raynor \(^3\) for powders quenched to room temperature from the single phase region.
It was found that the lattice parameter in the 'a' direction increased linearly with increasing antimony content. Measurements using an 11.46 cm Debeye-Schierer camera revealed no change in lattice parameter between deformed and solution treated powders (section 4.4.1). In this case it is considered that the failure to observe any change in parameter was due to insufficient resolution because of the small camera diameter. This was smaller than the 19cm camera used by Lee and Raynor, and hence any change in 'd' spacing would produce a correspondingly smaller displacement of line position measured on the film.

Greater resolution was available by using a diffractometer, and this also made possible the use of rolled flat strip specimens rather than powder. Difficulty was experienced, however, with finding suitable diffraction lines for lattice parameter measurement. The greatest change in diffraction angle with interplanar spacing is found at large values of \( \sin 2\theta \) (i.e. in back reflection) and hence it is these lines that must be measured for the greatest accuracy. Unfortunately in tin these lines also have a particularly low intensity so that peak shape may become distorted and the signal/noise ratio is poor. Under these conditions it is more difficult to determine the position of the centre of the peak than is the case for a strongly diffracting line. The Sn(400) line was chosen for study as it had a useful intensity but no change in lattice parameter was found between 30% and 90% deformed samples of 6% Sb pewter.
It must be concluded that in this case the change in diffraction angle with a very small change in lattice parameter was too small to be measured accurately and a different line at higher angle such as the Sn(620) was required. This line had a very low intensity, but lattice parameter changes were observed and are shown in Table 25.

It can be seen that for pure tin (0.02% Sb, 0.06% Pb) a parameter of $a = 5.816 \text{kX}$ was obtained at 25°C compared to a value of 5.820 kX determined by Lee and Raynor for 99.99% Sn at the same temperature. Since great care had been taken with the alignment of the diffractometer and frequent calibration checks made against a silicon standard these inconsistencies may have arisen from 2 other sources, namely the uncertainty in determining the exact centre of the peak as discussed previously, and systematic errors due to absorption of the X-ray beam, beam divergence and refraction. The latter effects are normally eliminated by plotting the apparent lattice spacings obtained from several line positions at high Bragg angles against a suitable function such as that determined by Nelson and Riley and extrapolating to $\Theta = 90^\circ$. In the present investigation a reliable determination of the interplanar spacing was only obtained at one Bragg angle so this technique was not available.
Since the accuracy of determining the centre of the peak was estimated to be $\pm 0.02^\circ$ (20) corresponding to an uncertainty of $\pm 0.001$ kX in lattice parameter, and any effects due to impurities being of lesser degree, it was concluded that the discrepancy in the 2 results was due to inherent systematic errors. To correct for this effect 0.004 kX was added to all the values measured so that the experimental value of ‘a’ for tin was in agreement with the results of Lee and Raynor. The correction will only vary with Bragg angle, and this is effectively constant for all the results in table 25. Comparing these adjusted results with those obtained by Lee and Raynor for quenched Sn-Sb alloy powders, matrix antimony concentrations of 1.8% Sb and 4.2% Sb are obtained for the 90% deformed and solution treated alloys respectively. Whilst the concentration of antimony in the matrix measured in the rolled specimen shows good agreement with results obtained from point counting of SbSn precipitates (1.5%), the solution treated value is less than the bulk concentration in the alloy (5.9%). This was a surprising result since the solution treated alloy has been shown to be substantially single phase by optical microscopy with very few SbSn precipitates at grain boundaries. Neither can the difference be accounted for by measurement accuracy since this would only amount to an uncertainty of $\pm 0.6$% Sb.
The source of this discrepancy is uncertain, but it may be speculated that either the remaining antimony is present as some sub-microscopic second phase, or that some unidentified source of error has entered into the measurement. Electron probe microanalysis has produced contradictory results for the analysis of matrix antimony concentrations that are highly dependant on the type of analysis used. It is now clear that the use of the energy dispersive specrometer which requires deconvolution of the spectra is unsuitable for the determination of small amounts of antimony dissolved in tin. This arises from two sources namely the slight drift in calibration of the multichannel analyser, and the high sensitivity of the deconvolution procedure to background counts when the antimony components of the complex spectrum are small. Analyser drift is usually very small, and in the analysis of elements whose X-ray spectrum does not overlap it is of no consequence. However when a small second peak has to be deconvoluted from a much larger overlapping peak extreme stability of calibration is required. Frequently this is not obtained in practice. Background noise is also a problem since this must be subtracted from the total of counts in each channel of the multi-channel analyser before deconvolution. Since noise is by definition 'noisy' it is not possible to give it a precise value.
However, the programme assumes that the background varies linearly across the spectrum and subtracts this amount from the spectrum before determining the mean energy position. Any divergence from its assumption in this procedure will cause correspondingly larger differences in the proportion of the antimony standard spectrum present in the complex spectrum.

These sources of error are only serious when one component is present in small amounts. When the proportions of the 2 components are approximately equal, then a much better accuracy is obtained, as in the case of the analysis of SbSn. More reliable results have been obtained by use of the wavelength dispersive (crystal) spectrometer. The greater resolution of this system permits the tin and antimony I\(\alpha\) emission lines to be resolved separately and hence deconvolution is not necessary. Table 27 shows results for a series of binary pewters. It can be seen that the scatter in individual results is small, and that the values determined for the matrix antimony concentrations are similar (2.2 - 2.85%) for a range of bulk compositions between 2 and 6% Sb. It was noted that these values are higher than those determined by other techniques such as X-ray diffraction, point counting and DTA which give values of between 1% and 1.8% Sb for the same range of bulk compositions. There are several possible reasons as to why microprobe analysis may give higher values, namely:-
(1) The presence of an oxide film on the specimen surface which contains approximately 20% Sb (measured by electron spectroscopy).

(2) The enrichment of the metal near the surface with antimony due to electrolytic etching. Just below the metal/oxide interface an antimony concentration of 12.5% has been measured by electron spectroscopy (Table 29).

(3) The uncertainty as to whether a subsurface precipitate is contributing to the analysis.

Errors due to (1) and (2) are unavoidable since it is necessary to etch the surface so that precipitates can be seen and their inclusion in the analysed region be avoided. Assuming the analysed volume to be $1 \mu m^3$ and the oxide film to be $1000 Å$ thick (section 4.6) then the oxide will contribute to only 1% of the analysed volume. Hence errors due to (1) will be small and contribute to an increase of 0.2% Sb in the analysis. The enrichment of the metal surface in antimony arises because tin atoms are removed at a faster rate than antimony atoms during the etching process. Whilst a high concentration of antimony exists just below the surface it is not known how the concentration gradient varies with depth, and hence the contribution to the overall accuracy of analysis cannot be estimated, but may be large.
The effect of sub-surface precipitates again cannot be estimated, however less scatter is seen in the individual results for the 2% Sb alloy where the precipitate dispersion is coarse, compared to the 6% alloy where the interparticle spacing is closer and hence there is a greater statistical chance of an SbSn particle contributing to the analysed volume. Where especially high antimony concentrations were encountered (~10%) the analysis was discontinued at that point as a sub-surface precipitate was suspected.

More reliable measurements have been obtained by microscopic examination and point counting. If the amount of SbSn present in the structure is known, then the matrix antimony concentration can be calculated. Table 25 shows that for a 6% Sb alloy the fraction of SbSn increases rapidly with rolling reduction up to approximately 70% deformation where values of 9.5% are obtained. Further rolling produces only a slight increase in the amount of precipitate.

Volume fractions of SbSn of 6.2% and 0.7% for the 4% and 2% antimony pewters in the 90% deformed condition correspond to matrix antimony contents of 1% and 1.6% respectively, whilst that for the 6% Sb alloy was found to be 1.5%. These values are in quite close agreement with the 1.3% antimony determined by D.T.A. for the 4 and 6% Sb alloys from the resolution start temperature, and the 1.8% determined by X-ray lattice parameter measurement of the 6% Sb alloy.
The large increase in the amount of SbSn present when pewter is subject to large rolling reductions is considered to be due to the increase in grain boundary area following recrystallisation which provides an increased number of sites for nucleation of the precipitate. The work of Lange et al. \((33,34)\) shows that the rate of grain boundary self diffusion at room temperature is some \(10^9\) times faster than matrix diffusion. It is reasonable to assume that a similar relationship holds for antimony diffusion in tin, and hence the growth rate of viable nuclei will be enhanced at the grain boundaries by this easy diffusion route. Also the distance between the grain centre and the grain boundary is greatly reduced giving a much shorter diffusion path to maintain the solute flux to the growing precipitate. In addition to the reduction in hardness due to the loss of solute from the matrix, precipitation also causes a refinement in the recrystallised grain size by preventing grain growth at room temperature. This effect can be predicted by the use of the Zener equation. \((78)\)

\[
\text{Max recrystallised grain size} = \frac{4\text{rp}}{3\text{Fv}}
\]

where \(\text{rp} = \text{mean precipitate radius}\)

\(\text{Fv} = \text{dispersed precipitate volume fraction}\)
This equation has been criticised by Wold and Chambers\(^{(79)}\) on the grounds that Zener's assumptions that all particles in contact with the boundary contribute the maximum possible pinning force is not compatible with the existence of known variations in boundary curvature, and that this average restraining force can be expected to be about half that suggested by Zener. In spite of these limitations it was expected that the recrystallised grain size would decrease with deformation as the volume fraction increased.

Using the values for the volume fraction of SbSn shown below, and a typical measured SbSn precipitate diameter of 2 \(\mu\text{m}\) the maximum grain sizes can be calculated for 90\% deformed specimens.

<table>
<thead>
<tr>
<th>% Sb</th>
<th>Fv</th>
<th>rp</th>
<th>Max G.S. (calc)</th>
<th>Measured G.S.</th>
</tr>
</thead>
<tbody>
<tr>
<td>6</td>
<td>0.092</td>
<td>1 (\mu\text{m})</td>
<td>13 (\mu\text{m})</td>
<td>2 (\mu\text{m})</td>
</tr>
<tr>
<td>4</td>
<td>0.062</td>
<td>1 (\mu\text{m})</td>
<td>22 (\mu\text{m})</td>
<td>4 (\mu\text{m})</td>
</tr>
<tr>
<td>2</td>
<td>0.007</td>
<td>1 (\mu\text{m})</td>
<td>200 (\mu\text{m})</td>
<td>11 (\mu\text{m})</td>
</tr>
</tbody>
</table>

Table 34 Calculated and Observed Grain Size in Rolled Pewter

Table 34 shows that the grain size of rolled pewter decreases with increasing antimony concentration as anticipated, but that the measured grain sizes are all less than that predicted by the use of Zener's equation. This does not, however, imply any inconsistency between theory and experimental results since the predictions apply to the maximum equilibrium grain size.
The implication is that the grain sizes measured in this investigation are non-equilibrium and will in time increase to the predicted size (or larger) by grain growth at room temperature. Experimentally it was found that no measurable grain growth had occurred in the same specimens between examination soon after rolling and subsequent measurement several months later, however no comment can be made at present concerning changes that may occur many years in the future.

A temperature of 80°C was used to deliberately coarsen the structure of a 6% Sb alloy by heat treatment for a period of 10 days. The average precipitate radius increased to 3μm as a result of this treatment, but the volume fraction of precipitate remained essentially unaffected since the temperature was below that required for resolution of the SbSn. A new maximum grain size of 40 μm was predicted for the coarse particulate structure. Microscopic examination showed a mixed grain size, where 20% of the grains were of 40 μm diameter, and the remainder 90 μm. This discrepancy may be explained in terms of the criticisms of Wold and Chambers (79) as the kinetics of grain growth are faster at this elevated temperature than is the case at room temperature considered previously.
5.3 The Properties of Rolled Pewter Sheet

5.3.1 Room Temperature Properties

Since rolled sheet accounts for much of the present consumption of pewter, and is the condition in which "work-softening" causes serious problems, much effort has been directed towards mechanical testing which provides both order of merit ranking on various compositions, and also provides information on the mechanism by which hardness reduction occurs. Testing of the first kind has been mainly confined to Vickers hardness tests, while mechanistic tests have been carried out under conditions of varying load or strain rate.

Figures 11 and 12 show the hardnesses of the binary and ternary pewters investigated in the 90% deformed condition. This deformation corresponds approximately to the total deformation experienced under industrial practice, and the results are relevant to commercial sheet production. It can be seen that the hardness of rolled pewter increases with increasing antimony content, but the hardening effect of copper additions are much smaller in this condition than is the case for cast ingots. In contrast the addition of copper to pure tin increases the hardness from 6.5 Hv to 13.5 Hv at 90% deformation.
This apparent inconsistency can be best accounted for by considering the nature of the Vickers hardness test, which is essentially a high strain rate compression test during the period of indentation followed by a compressive creep test under conditions of decreasing stress. With a complex test of this type the hardness measured is a composite parameter which reflects the material's resistance to deformation under two widely differing sets of conditions. Whilst for the vast majority of engineering materials at room temperature this distinction is unimportant, for pewter, which exhibits a low creep resistance and a high strain rate sensitivity the Vickers hardness test is not a true reflection of any one particular material property. Less ambiguous information can be obtained by measuring the flow stress over a range of strain rates. This provides meaningful data for the resistance to deformation and also gives a strong indication as to the deformation mechanism. Figures 29 and 30 show plots of the true flow stress at 1% strain as a function of strain rate between $1.25 \times 10^{-3}$ and 5 per minute for tin/6% Sb and tin/6% Sb/2½% Cu in the 90% deformed condition. It can be seen that the curve obtained can be divided into two separate regions.
virtually a straight line of slope 0.25, whilst at high strain rates (>5 × 10⁻¹/minute) another straight line is obtained of much lower slope (<0.1). Between these two lines there is a curved transition region of gradually decreasing slope.

From the work of Alden and others this type of behaviour is seen to be very similar to that shown by superplastic materials which exhibit a sigmoidal variation of σ with ° (Fig 35).

The low strain rate portion, up to 2.5 × 10⁻²/minute, is creep, and deformation.

Although that which does exist suggests that Nabarro-Herring creep may be playing an increasingly important role in many alloy systems region I is absent.

The region of maximum strain rate sensitivity (region II) with slope of m > 0.3 delineates the strain rate range over which superplasticity occurs. Both the low and high regions exhibit values of S.R.S. (=m) of 0.1 although in many alloy systems region I is absent. (60)
Studies of materials deformed in region III show that slip lines can be observed on the surface \(^{(64, 65)}\) and a high density of dislocations is visible within the grains \(^{(80, 81)}\) and in addition some grain boundary sliding is observed. It is therefore generally agreed that deformation in this region involves slip and recovery creep. Plate 25 shows the presence of surface slip bands after deformation at a strain rate of 12.5/min (region III), but no obvious grain boundary sliding was observed at fiducial surface scratches. Coarse surface slip bands were particularly noticeable in the case of the 6% Sb alloy that had been subject to a grain coarsening heat treatment (plate 37).

Region II, in which grain boundary sliding predominates, has been reviewed in section 2.4. Boundary sliding is shown to provide an alternative deformation mechanism which operates at a lower applied stress than that required for slip or recovery creep in Region III, at low and intermediate strain rates in fine grained material at a temperature within the creep range.

Superplasticity is generally agreed to be limited to the range of behaviour where \(m > 0.3\), although reviews of the literature show a range of \(m\) values from 0.2 to 0.85 where the phenomena still occur.
Results in this investigation for 6% Sb binary and ternary pewters give typical m values of 0.25 with tensile elongations of 150% at the lowest strain rates used. Whilst the values are lower than those usually encountered in superplastic materials, the form of the log $\sigma$/ log $\dot{\varepsilon}$ plots, the relatively high elongations obtained with diffuse stable necks, and the observed rotation and offset of fiducial marks at grain boundaries (plate 20), all indicate that superplastic deformation makes a significant contribution to the overall deformation strain.

The reasons are not completely understood for the low m values and rather limited ductilities in such a fine grained material, which otherwise shows all the characteristics of superplasticity. The majority of results reported in studies of superplasticity are obtained on eutectics, eutectoids, or other multiphase alloys where the properties of the two phases are similar, and both undergo limited deformation to maintain boundary contact. Conversely in rolled pewter the fine grain size is established by hard particles in the grain boundaries of a much softer matrix. Therefore if relative sliding is to occur between adjacent grains which contain a precipitate particle on their common boundary, accommodation processes must allow material to flow past the precipitate rather than the precipitate deforming.
Results from the literature show a lack of agreement concerning the effect of hard particles on superplastic deformation. Yowder and Weiss\(^{(83)}\) found that a spheroidised pearlitic steel gave a value of m = 0.42 when deformed at 716°C, but with a relatively small elongation of 133%. Schadler\(^{(83)}\) also found evidence of superplasticity in an ultra fine grained 0.4% carbon steel, but only when tested in the α + γ region (727°C). On testing at 662°C (0.51 Tm) in the α + Fe₃C phase field m was reduced from 0.65 to 0.12 with a ductility at failure of 80%.

The effects of small silver additions to the lead-tin eutectic, a material well known for its superplastic behaviour, have been studied by Humphries and Ridley\(^{(84)}\). This had the effect of introducing fine hard particles of Ag₃Sn at the grain boundaries. The initial grain size was 2 μm and strain rates of $10^{-2.5}$ to $10^{-0.5}$ per min were investigated. The silver additions were found to reduce the strain rate sensitivity from 0.53 to 0.4, and cause a large reduction in the failure strain due to cavitation around the Ag₃Sn particles. In addition the flow stress at constant strain rate was increased when the particles were present. Sagat and Taplin\(^{(85)}\) have concluded that in alloys which do not cavitate the flow has been characterised by two instabilities. Quite early in the test one or more diffuse necks develop in the specimen gauge length.
The second instability develops much later and involves the rapid and preferential growth of one neck, and the material separates to a point. In alloys which cavitate the formation of intergranular cavities hampers the flow and causes premature failure. The presence of stable diffuse necks and the absence of voids or decohesion around SbSn precipitates in the body of failed specimens of binary alloys confirms that cavitation does not occur during deformation in region II. Cavitation is also absent near the final failure where the local strain rate is high and will correspond to region III (plate 20). Ternary alloys show extensive cavitation in the neck region, (plate 21) but this has not been detected elsewhere in the gauge length. Although these comparisons are inconclusive it is suggested that the lower m values exhibited by pewter, in comparison with other superplastic materials, reflects the difficulty of material flow around SbSn particles. Accommodation processes such as diffusional creep, localised dislocation movement by glide and /or climb or a combination of these, permit the local plastic flow without the nucleation of voids which would lead to early failure.

Figure 31 shows log σ/log ε plots for 90% deformed binary pewter alloys containing 2, 4 and 6% Sb. These form a family of curves of the type already discussed which are displaced to higher stresses at higher antimony contents.
The grain sizes of these alloys were 11 μm, 4 μm and 2 μm respectively. It is interesting to note that although the grain size and volume fractions of precipitate vary systematically throughout the 3 compositions the strain rate sensitivities and the transition strain rate between region II and region III behaviour are similar. This is an unexpected result since in general a smaller grain size tends to give a higher S.R.S., and region II behaviour is maintained to a higher strain rate and at a lower flow stress than would be expected for a coarser grained material. However, when the effects of the precipitates are considered it can be seen that the larger volume fraction of SbSn which accompanies the smaller grain size would tend to increase the flow stress and decrease the strain rate sensitivity as found by Humphries and Ridley (84), and also by Raj and Ashby (86) in their study of the torsional shear of grain boundaries containing Al₂O₃ and SiO₂. In addition there would be a tendency to decrease the transition strain rate as grain boundary sliding becomes more difficult due to the larger number of obstacles in the boundary. Taken together the effects of grain size and precipitate volume fraction tend to cancel each other out, and hence explain the similarity of the 3 curves in figure 31.
These results are contrary to the findings of Alden for a tin-5% Bi alloy, which has a very similar microstructure to Sn-Sb alloys. These alloys were warm extruded in the single phase region and immediately quenched into liquid nitrogen to retain a very fine grain size. Before testing the specimens were aged at room temperature for varying times to allow particles of Bismuth to precipitate at the grain boundaries and to give time for grain growth. By this method grain sizes between 1.2 μm and 16 μm were obtained, and a strong dependance of flow stress on grain size was noted. In addition the transition between region II and region III behaviour was shifted to higher strain rates for the fine grain size alloys.

In this case the particles appeared to play very little part in controlling the deformation, however it seems doubtful that the particle size and volume fraction were constant for all grain sizes. In particular for the shortest annealing times and finest grain size precipitation appears to be incomplete and the particles very fine.

In order to study the combined effect of particles and a change in grain size, test pieces of 90% deformed Sn/6% Sb alloy were given a heat treatment of 80°C for 10 days. Differential thermal analysis has shown that precipitates do not redissolve at this temperature.
Also the temperature is just below the α/α + SbSn phase boundary as determined by Eyre\(^{(33)}\), for the measured matrix antimony content (1.3 - 1.8% Sb). Hence neither resolution nor further equilibrium precipitation would be expected. The effect on the microstructure was to allow the grain size to coarsen to 90µm from an as rolled grain size of 2 µm. The effect of this treatment is shown in figure 29, over the same range of strain rates used for the as rolled alloy. The plot of \(\log \sigma/ \log \dot{\varepsilon}\) is linear at all strain rates and typical of region III behaviour, region II having either disappeared completely as a result of the coarsened grain size, or been moved to much lower strain rates which were beyond the range of this investigation. These tests confirm that the high S.R.S. and poor creep resistance of rolled pewter at low strain rates result from grain boundary sliding due to the fine recrystallised grain size, and is not simply due to the loss of solid solution strengthening. At high strain rates, the low strain rate order of merit is reversed as seen in figure 29. In region III the strain rates are too fast for grain boundary sliding to make any significant contribution to the testing strain, and at the highest strain rates recovery creep is also negligible. Hence the factors controlling strength are those that control conventional plasticity and dislocation movement, and in this instance the most important variable appears to be grain size.
Comparing the traces for the as rolled alloy and the coarsened alloy in figure 29 it can be seen that for constant matrix antimony content the fine grained rolled alloy has a much higher flow stress than the same alloy after a heat treatment at 80°C for 10 days. This is the expected behaviour at this strain rate due to the strengthening effects of the grain size as predicted by the Petch relationship:

\[ \sigma_y = A + Kd^{-\frac{1}{2}} \]

\( \sigma_y \) = yield stress (Mpa)

Where A and K are constants and

\( d \) = grain size (metres)

For the 6% Sb alloy as rolled, and after coarsening, and also for the rolled 2% Sb alloy the expression \( \sigma_y = 52.5 + 2.8 \times 10^{-2} d^{-\frac{1}{2}} \) provides a fit within 2% for the 1% proof stress at a strain rate of 1.25/min

<table>
<thead>
<tr>
<th>Composition</th>
<th>Treatment</th>
<th>Grain Size</th>
<th>( \sigma_y ) calc</th>
<th>( \sigma_y ) exptal.</th>
</tr>
</thead>
<tbody>
<tr>
<td>6% Sb</td>
<td>As rolled</td>
<td>( 2 \times 10^{-6} ) m</td>
<td>72.5</td>
<td>72</td>
</tr>
<tr>
<td></td>
<td>Coarsened</td>
<td>( 9 \times 10^{-5} ) m</td>
<td>56</td>
<td>55</td>
</tr>
<tr>
<td>4% Sb</td>
<td>As rolled</td>
<td>( 4 \times 10^{-6} ) m</td>
<td>66.5</td>
<td>59.5</td>
</tr>
<tr>
<td>2% Sb</td>
<td>&quot;</td>
<td>( 11 \times 10^{-6} ) m</td>
<td>60.7</td>
<td>60</td>
</tr>
</tbody>
</table>

Table 35 Calculated and Experimental values of Flow stress (MPa.) in Pewter at \( \dot{\varepsilon} = 1.25/\text{min} \)
The measured flow stress for the rolled 4% Sb alloy is a little lower than the calculated value. Sheet rolled from this ingot has been shown to have a matrix antimony content 0.5% Sb less than either the 6% Sb or the 2% Sb alloys. It is suggested that this behaviour is specific to this particular ingot and rolling schedule, and not an effect general to all 4% Sb alloys. The effect would be to decrease the resistance of the alloy to slip controlled deformation due to a decrease in solid solution strengthening, as observed above.

5.3.2 Creep Properties of Tin and Rolled Pewter

At high temperatures the rate of creep of most metals and many solid solution alloys is controlled by the recovery of the dislocation substructure. When the homologous temperature is in excess of from 0.55 to 0.7 of the melting point dislocation climb appears to be the rate controlling recovery process, and consequently the rate controlling process in creep. The rate of dislocation climb creep depends upon the dislocation substructure that is present in the metal. Eventually a steady state is achieved in which both the creep rate and the rate controlling substructural details remain constant.

Although other empirical functions have been suggested, the steady state creep rate can usually be represented as a power of stress and a temperature function:-

\[ \dot{\varepsilon} = A \sigma^n e^{-\frac{Q}{RT}} \]

Which is the form of equation used in section 4.10.
The values of n for creep vary from about 3 to 7 for various solid solution alloys and pure metals. Most frequently pure metals give values of between 4.2 and 6.9 \(^{(87)}\). This has suggested an average value of 5 \(^{(88)}\) for dislocation climb.

Tensile creep tests, and tests involving variable time hardness tests show similar results to those obtained in constant strain rate tests at low testing speeds. This is to be expected provided that the stresses measured in the constant strain rate tests, and the S.R.S. values \(m\) calculated, are those obtained under conditions of steady state creep.

This was found to be so since the primary creep period in pewter is very short as can be seen from figure 10, and occupies only the first \(3/4\%\) \(\varepsilon\) in the range of strain rates investigated. After this strain the true flow stress is constant. Since the strain rate sensitivity is obtained by back extrapolation from a period of secondary creep the same argument applies.

i.e. since \(\sigma = K \dot{\varepsilon}^m\) at constant temperature

and \(\dot{\varepsilon} = K^{-1} \sigma^n\)

then \(n = \frac{1}{m}\)
Clearly the identity above is not obeyed if the conditions under which the data was collected were not be the same. Tensile creep testing of pure tin yields values of $n$ of 6.1 and 6.6 (Table 31) depending on grain size, whilst higher values of $n = 7.5$ are obtained from hardness testing (table 30) using the analysis of Murty et al. These values may be compared with $n = 9.3$ obtained by applying the same analysis to the hardness data produced by Hargreaves for pure tin which had been cold rolled. In general the results of tensile creep tests are to be preferred to those results obtained from hardness tests where the load is maintained for varying time intervals, since in the former the stress distribution is known to be uniform across the whole cross-section. With hardness testing certain assumptions need to be made concerning the stress distribution in the vicinity of the indenting ball, which have been empirically extended to the case of Vickers hardness testing. Whilst this method has shown good agreement with tensile creep results in some other materials, particularly those showing superplasticity, it has not been demonstrated that this agreement extends to all situations where the creep mechanism may be different, and hence where the degree of plastic constraint of the surrounding material may also vary.
Cline and Alden\(^{(89)}\) reported strain rate sensitivities of 0.125 \((n = 8)\) in differential strain rate tests on pure tin with a grain size of 45 \(\mu m\). When the grain size was reduced to 7 \(\mu m\) by extrusion under carefully controlled conditions the material exhibited as S.R.S. of 0.5 \((n = 2)\) at a strain rate of \(10^{-3}/\text{min}\). The flow stress was determined "when the steady state was approached", so it is possible that the \(n\) values obtained for the coarser grained material does not correspond exactly to steady state creep. Also it was noted that for the 7 \(\mu m\) tin, grain growth occurred during the test. The values of \(n = 6.1 - 6.6\) obtained in section 4.8.2 are higher than those usually obtained in F.C.C. metals which creep by dislocation climb. In contrast to the F.C.C. metals the values of \(n\) for B.C.C. and hexagonal metals vary much more widely from 4 to 7.\(^{(87)}\) No data was presented in this review for tin (B.C.T.) but it may be presumed that tin deforms by the dislocation climb mechanism, which is the most common mechanism for metals at high homologous temperatures that do not have especially fine grain sizes. The value of \(n = 7.5\) obtained in section 4.8.1 by hardness testing is outside the range of values normally encountered, although it does show a good correlation with the results of Cline and Alden. However the comments already made concerning hardness testing make the tensile creep results preferable.
Tensile creep testing of rolled Sn/6% Sb and Sn/6% Sb/2½% Cu alloys give values of the stress exponent (n) of 4.1 and 4.8 respectively (section 4.8) whilst tensile tests at variable strain rates gives n = 4.6 for both compositions (table 33). These results show n values less than those for pure tin and hence show the effect of significant grain boundary sliding on the creep strain at very fine grain size. The reason for the decrease is that superplasticity is characterised by a stress exponent (n) of 2-3 instead of 4-7 for dislocation climb. The results of Cline and Alden \(^{(89)}\) for tin with a 7 μm grain size suggest that 6% Sb and 4% Sb pewter which also have a fine grain size of 2 μm and 4 μm respectively should behave as superplastic material with a lower n value (or higher strain rate sensitivity) than that measured, if it were not for the effect of the SbSn precipitates on reducing the rate of grain boundary sliding.

5.3.3 Mechanical Tests between +70°C and -40°C

Differential strain rate and monotonic tensile tests were carried out to investigate the effects of strain rate and temperature on the ductility of pewter and determine the relationship between ductility, strain rate sensitivity and temperature. In addition the activation energy for creep was determined for pure tin, and rolled pewter under conditions where the strain rate sensitivity was high.
Figure 32 shows the elongation at failure for a rolled tin/6% Sb alloy between 20°C and -40°C at a variety of strain rates. Scanning electron micrographs of the failures are also shown in plates 20-35.

At room temperature the ductility at low strain rates is high (150%) with an S.R.S. of 0.24. Increasing the strain rate above $1.25 \times 10^{-2}$/min results in a decrease in S.R.S. with a dramatic decrease in ductility as the end of region II behaviour is reached. This may be compared with the consistently low ductility of the same alloy after a grain coarsening treatment at 80°C for 10 days where only region III deformation occurs.

Reducing the temperature to -10°C results in a curve of similar shape but with an overall decrease in ductility. At -40°C a constant low ductility is obtained. Micrographs of the fracture surface show that chisel point fractures are formed where the ductility is high, indicative of the effects of some superplastic behaviour. As the ductility decreases due to temperature or strain rate, the appearance of the fracture changes to a blunt failure with a typical ductile dimple structure obtained by the coalescence of microvoids formed at triple points. In addition 45° shear bands can be seen on the side faces of the specimen showing the presence of large scale slip. This is much less noticeable in the high ductility specimens (region II).
Examination of the chisel point failures at high magnification shows the presence of large voids which frequently show intergranular separation within the void interior. Sectioning of failed specimens for optical metallography shows that these are only present at the fracture surface in binary alloys, and also within the necked region of ternary alloys subject to region III deformation. An examination of the fracture surface of an Al-Cu eutectic alloy after superplastic deformation has shown a very coarse ductile failure where the "dimple" size is much larger than the grain size raised to the power of 90 produced by the separation of clumps rather than individual grains. In the pewter alloys examined (plates 23-38) this mechanism does not appear to be present as the voids are very deep relative to their width, also no groups of grains can be seen in relief on the surface of a comparable size to the voids. Instead it is proposed that these voids are formed ahead of the propagating crack front by a co-operative sliding process, and are nucleated by cavitation of grain boundaries oriented normal to the direction of maximum principal stress, as is frequently found in tertiary creep.

Figure 34 and table 33 show the results of tests to determine the activation energy for the deformation of tin and pewter at strain rates between $1.25 \times 10^{-3}$ and $2.5 \times 10^{-3}$/min.
Values of the activation energy for the creep of pure tin determined in this investigation (21.3 - 22.3 K cal/mole) compare well with those determined by Frenbel, Sherby and Dorn (21 ± 2 k cal/mole) under conditions of constant stress. However it should be noted that the value of n = 11.1 used in the present calculation was obtained from the slope (m = 0.09) of the constant strain rate results, and is at variance with the results of constant load tensile creep tests (n = 6.1 - 6.6).

It is suggested that this discrepancy arises from the relatively long period of primary creep found in pure tin, compared to that found in rolled pewter. Thus at 1% strain, the point at which the strain rate change is made, the flow stress is still slowly increasing and the test is carried out under conditions which do not strictly correspond to steady state creep. Conversely the tensile creep tests are carried out at rather larger total strains where the minimum creep rate has been established. If the strain rate changes had been made later in the test then a greater difference in the flow stresses would have been measured and the value of the strain rate sensitivity correspondingly increased.

In turn a lower value for n would be obtained, closer to that found in the constant load creep tests.
The significance of the results obtained are open to some question since they are a measure of the activation energy for the latter stages of primary creep rather than for steady state creep.

The major substructural changes occurring during transient (primary) creep were pointed out by Gupta and Strutt to centre on the dispersal of dislocation entanglements, but the relationship between such dispersal and the transient creep rate is not yet understood. It was further noted that all substructural changes during high temperature transient creep are interrelated and dependant on the dislocation climb mechanism. Amin et al therefore suggested that transient creep as well as steady state creep is controlled by the rate of climb of dislocations. Since the rate controlling mechanism is the same in both cases the similarity between the activation energy determined in section 4.10 and the steady state values determined by Frenkel et al is expected.

The activation energy for the creep of Sn/6% Sb in the 90% deformed condition at low strain rates was found to be 16 (+2) K cal/mole (table 33). This is less than the value for coarse grained tin which deforms by the dislocation climb mechanism and has an activation energy of 21 K cal/mole or 22 K cal/mole (section 4.10). The reasons for this is that the pewter alloy has the additional contribution of grain boundary sliding to the observed creep rate.
Since the rate controlling process for this is grain boundary mobility, the activation energy would be similar to that for grain boundary diffusion\(^{(60)}\). Thus if deformation was achieved totally by this mechanism values of \(Q = 9.55 \text{ K cal/mole}\) would be expected.\(^{(34)}\) The observed values fall between those predicted for the two mechanisms and suggest that slow deformation in rolled pewter is a mixed mode process. This view is further supported by ductilites which are larger than those obtained in conventional creep failures, but less than the many hundreds of percent elongation frequently reported for superplastic failures. In addition, when the extent of grain boundary sliding is severely limited by grain coarsening at 80°C, the ductility falls from 150% to approximately 60%.

5.4 Tests on Solution Treated Pewter

Frequent reference has been made to the beneficial effects of a heat treatment at approximately 200°C on the hardness of pewter. This is particularly true of pewters that contain copper where the amount of softening on rolling is large and the corresponding hardening on heat treatment is more pronounced than in binary alloys which have similar hardnesses in the rolled and solution treated condition.
Figure 29 shows the log $\sigma$/log $\dot{\varepsilon}$ plot for 6%Sb pewter, solution treated at 225°C, in addition to the plot for the rolled alloy. It can be seen that a perfectly linear response is obtained which intersects the rolled line at a strain rate of $2.5 \times 10^{-2}$/min. Similar explanations can be advanced for this behaviour in terms of grain size as in the case of the coarsened rolled alloy discussed in section 5.3.1. At high rates the strengthening effects of grain boundaries predominate, the much smaller grained rolled alloy shows a higher flow stress. At low strain rates the alternative deformation mechanism of grain boundary sliding results in a much lower flow stress. Although the behaviour of the material in the two conditions is very different, the effects are combined in a hardness test to give a very similar hardness value.

Comparing these results to fig 30 for the Sn/6% Sb/2.5% Cu alloy it can be seen that although the rolled materials behave almost identically, the line for the copper containing solution treated material is displaced to higher flow stresses. In all other respects however, it is similar to the line for the binary alloy. This displacement is the result of the interstitial solid solution strengthening from the copper and also some contribution from the dispersion of Cu$_6$Sn$_5$.

The rolled and solution treated trace intersect at a strain rate of $2 \times 10^{-1}$/min, and the flow stress difference at the
higher strain rates typical of hardness indentation is much smaller than is the case in the binary alloy. Hence the resistance to deformation is greater in the case of the solution treated alloy for a wider range of conditions and a higher hardness is found. In tests which give a large weighting to high strain rate properties such as the Shore Scleroscope the hardness of pewter was found to increase with rolling reduction, whereas Brinell testing, particularly at long indentations times, tended to give more weighting to the creep strength of the material and a decreasing hardness observed. This effect was noted by Edgeberg and Smith for a 7% Sb, 2% Cu alloy, but not explained, and they considered the Scleroscope results to be erroneous. (Table 6)

Creep testing of solution treated or partially solution treated pewters confirms the superior creep resistance of these alloys which do not show the deleterious effects of grain boundary sliding. In particular the plots of log secondary creep rate against log stress (figure 28) are characterised by a very high dependance of strain rate on stress which is the exact opposite of the behaviour of rolled alloys. Table 32 shows that the stress exponent (n) has very high values in the range 11 - 16 for solution treated 6% Sb and 6% Sb/2½% Cu alloys.
These stress exponents are much higher than those obtained in pure tin and it is difficult to explain them in terms of dislocation climb.

One possible contribution to the high n values is the observation that in F.C.C. metals at least, the value of n increases systematically with the inverse of the stacking fault energy \(93\). It was commented that it appeared likely that the stacking fault energy has the same effect on the steady state creep rates of F.C.C. alloys which undertake the dislocation climb mechanism as it does for the F.C.C. metals. As it is generally observed in most metals that stacking fault width increases with alloying this should be accompanied by a decrease in creep rate and a small increase in n.

Whilst the effect of stacking fault energy may make some contribution to the high n values in pewter it would not appear likely that it could account for values as high as 11 - 16. One area in which anomalously high n values have been reported is for the high temperature creep of dispersion alloys. Mukherjee \(87\) has commented that the creep deformation in these alloys is often a complex phenomenon that is not well understood, and the behaviour is so sensitive to the type and nature of the dispersion that different processing histories often lead to creep by entirely different mechanisms even in the same alloy. Observations of n values as high as 40 have been made by Wilcox and Clauer \(94\) for the creep of thoriated nickel containing particles between 200 and 1000Å.
Abnormally high stress exponents have also been obtained by Haberlin (95) in age hardened steels containing niobium. Here solution treated alloys showed n values of 4-5, which increased to 9-10 on peak ageing. Gross overaging resulted in a decrease to n = 4-5.

In addition to their effect on the stress exponent dispersion, alloys often show experimental activation energies for creep which are several times higher than that for self diffusion (96). This was also found by Wilcox and Clauer (94) who noted that there was as yet no theory which satisfactorily explains the stress and temperature dependence of materials such as these.

To examine the hypothesis that solution treated pewter might be a dispersion alloy rather than being single phase, electron microscopy was carried out on extraction replicas obtained from solution treated 6% Sb pewter. Before replication the alloy was rolled 20% to peak hardness to encourage any strain induced precipitation that might occur. Previous attempts to produce thin foils for direct observation had been unsuccessful (section 3.6.2) and replication provided the only technique available, although direct observation would have been preferred if it had been possible. The disc shaped precipitates shown in plate 13 do not appear to show any crystallographic relationship to the parent phase. Thus if there are genuine precipitates they would be incoherent. Plate 14 shows a very different structure from the same specimen which has the same crystal structure as the precipitates in plate 13.
Clearly this is not a precipitate extracted from the matrix but appears to be an oxide stripped from the surface. The exact nature of these oxides is uncertain. The electron diffraction pattern is very similar to that of Sb$_2$O$_3$ (table 27), however, analysis of the oxides by E.P.M.A. shows that only 20-25% Sb is present, the balance of the metallic atoms being tin. E.S.C.A. analysis of the etched metal surface confirms that a surface oxide approximately 100Å thick is present, with antimony forming 20% of the metal atoms. It is unlikely that a complex oxide containing tin-antimony ratios of 4:1 would be isomorphous with Sb$_2$O$_3$, and a more probable explanation is that the tin and antimony are present as separate oxides. No diffraction spots from any crystalline tin oxide have been obtained, so it is possible that either this oxide is amorphous, or the spots have passed unnoticed as diffraction is very weak due to the thinness of the oxide film, unless large areas are involved such as in plate 14. Although the nature of the oxide is uncertain the shapes of the discs in plate 13 are very similar to those of incoherent precipitates in many alloy systems, and it is necessary to consider why oxides of this morphology should be present in the extraction replica. Other similar examples exist in 90% deformed alloys which are definitely associated with grain boundaries (plates 15 and 16), and it may be possible that the extracted oxides are the remains of precipitates which were oxysdised during the etching process.
Thus the grain boundary "precipitates" in plates 15 and 16 may have arisen from genuine precipitates such as those shown in plate 10. By a similar argument it is conceivable that the "precipitates" in plate 13 may have arisen from metastable matrix precipitates formed in lightly deformed alloys. These precipitates are not found in replicas taken from heavily deformed alloys and may have redissolved as a result of recrystallisation, to be re-precipitated as coarser SbSn.

Against this hypothesis must be set the facts that X-ray diffraction has failed to find any phases apart from the matrix in cast and solution treated binary alloys, the very small amount of grain boundary SbSn being below the detection limit of the technique. In lightly deformed alloys SbSn is detected in addition to the matrix, but here it is not possible to draw any distinction between grain boundary SbSn and any postulated fine dispersion of SbSn within the grains. Whilst the latter might be expected to give a broadened diffraction peak due to their fine size, no broadening was detected in SbSn lines at low deformation, and no other phases than the matrix and SbSn were detected in any binary alloy at any deformation.

If a precipitated phase apart from SbSn is produced it must either have a very low volume fraction below the detection limit of X-ray diffraction, or be structurally similar to the matrix phase.
In the former case it is most unlikely that such a small amount of dispersed phase would be able to exert such a large effect on the creep properties, and the latter case would appear to be incompatible with the high homologous temperature as structural instability and coarsening would be expected. Also thermal analysis shows no indication of any precipitation reaction on cooling solution treated material, nor any resolution on subsequent reheating, and hardness testing reveals no significant difference between alloys tested immediately after water quenching and those slowly cooled from the single phase region.

These findings appear to deny the existence of age hardening precipitates in undeformed solution treated pewter, but the question still remains as to whether such precipitation can occur when the material is subject to small strains during a creep or tensile test and cause the formation of SbSn on a much finer scale than has previously been observed at the grain boundaries. Electron microscopy of extraction replicas does not provide definite evidence either way since the only precipitates observed have been oxides whose exact structure is uncertain. Whilst these may have formed from pre-existing age hardening precipitates this cannot be proved, and the known enrichment of the metal surface in antimony by the etches used in this investigation may render them atypical of the bulk with regard to any precipitation processes.
In spite of these objections the high values of stress exponent and high activation energies found in creep tests on solution treated pewter are, at the present time, only explicable in terms of a dispersion strengthened model.

It would appear difficult to design a definitive experiment to decide this point short of the direct observation of precipitates in thin foils of pewter. This has proved impossible so far since no satisfactory method has been found for electropolishing pewter, and ion beam thinning has been shown to cause an abnormal SbSn precipitation which would invalidate the results. Under these conditions it is difficult to be dogmatic as to the existence or non-existence of age hardening precipitates, but on balance there appears to be a greater body of evidence for the precipitates in terms of the creep results than there is to the contrary due to the negative results of microscopy and X-ray diffraction, however alternative preparation procedures will be required for transmission electron microscopy before this question can be definitely decided either way.

Tensile testing of solution treated pewter has been carried out at low strain rates and room temperature. This shows a completely different type of failure to the rolled alloys, and a chisel pointed fracture results at a low failure strain (plate 39).
In this case deformation is accomplished by large scale slip which is seen as a single shear zone which develops diagonally across the neck and a distinct offset is seen in the specimen. To restore axially a complimentary shear zone develops, leading to the formation of a V shaped trough of new surface on the specimen. This process of repeated shear is continued until the trough is propagated through the thickness of the specimen and failure results. The shear zones can be seen clearly in plate 41, and the failure is very similar to that reported by Weinrich and French (97) for copper and alpha brass. The steps involved are reproduced from their paper and are shown schematically below.

5.5. Development Alloys

The principles governing the choice of alloy composition for further study were basically those of grain size control and solid solution strengthening.
This investigation has shown that the softening of pewter alloys after rolling is due to a loss of solid solution strengthening and the drastic reduction of grain size on recrystallisation which is stabilised by the grain boundary precipitate. Clearly any replacement alloy should aim to achieve the maximum stable amount of solid solution strengthening with only a small amount of second phase in the form of fine precipitates. In addition the grain size should be fine enough to obtain the maximum benefit from grain boundary strengthening at high strain rates whilst not being so fine as to permit grain boundary sliding to occur to any significant degree in service. The solid solution strengthening of tin is confounded in most instances by its very small solid solubility for other elements, and great restrictions are placed on possible replacements for existing pewter compositions by this. In order to determine the alloy compositions which might be suitable for further study an examination was first made of the factors that influence the solubility and solid solution strengthening in tin based alloys.

The physical, chemical and mechanical properties of metallic solid solutions are all known to be affected by the difference in atomic size between the solvent and solute atoms. This correlation is also recognised in the factors formulated by Hume-Rothery to explain the solid solubility of alloying additions in cubic metals, and more specifically in F.C.C. structures. (98)
The problems of defining the size of an atom has been dis-
cussed by King (99), in which it is shown that two comple-
mentary methods of measuring atomic size are of value. 
One of these makes use of the closest distance of approach 
of the atoms in the structure of the pure elements this 
provides the only reliable criteria for applying the Hume-
Rothery 15% rule (98). The alternative approach is to 
derive a volume size factor from the effective volume of 
the solute atom in the context of the solid solution (100).  
Although the latter approach is of little value in 
predicting new possibilities for extensive solid solutions, 
it is related directly to the strain energy introduced into 
the solution by the solute atoms, and is therefore a suitable 
parameter for assessing the influence of size effects on the 
properties of known solid solution alloys. 
The atomic volume Ω of a metal or solid solution is defined 
as the mean volume per atom. The definition of the volume 
size factor, Ω_{sf}, rests on the observation that at low values 
of fractional composition (c) the atomic volumes of solid 
solutions vary linearly with the atomic concentration of the 
solute. The effective atomic volume (Ω_B) of a solute B is 
obtained by a linear extrapolation of the volume plot to 
100% solute, and using this value the volume size factor is 
defined as (99):-

\[ \Omega_{sf} = \left( \frac{\Omega_B - \Omega_A}{\Omega_A} \right) \]  

(1)
For many applications it is more convenient to use a linear derivative of the size factor. In order that such a linear size factor (l.s.f.) may retain all the properties of the sf, it is defined in terms of the Seitz radius, where

\[ r = \left( \frac{3n}{4\pi} \right)^{\frac{1}{3}} \]

\[ (l.s.f.) = \left( \frac{r_{0B}^* - r_{0A}^*}{r_{0A}^*} \right) \]

This size factor is calculated from the effective atomic volume of the solute using the relationship:

\[ (l.s.f.) = \left( \frac{\bar{\Omega}^B}{\bar{\Omega}^A} \right)^{\frac{1}{3}} - 1 \]

Since the change in \( \bar{\Omega}^B \) has been shown to be linear with concentration up to certain limiting concentrations, which depend on the particular binary system under consideration, the linear size factor can be used as a direct indication of the degree of solid solution strengthening that would be expected in a metallic binary system. According to Cottrell\(^{101}\), the effect of this interaction on the increase in yield stress is given by:

\[ \sigma_y = 2.5\mu \left( \bar{S} \right)^3 C \]

Where \( \mu \) = shear modulus

\( C \) = concentration

\( \bar{S} = l.s.f. \) as defined in equation (3)
The table below shows the maximum equilibrium solubilities for various alloying additions to tin and the increase in yield stress that would be expected on the basis of the Cottrell model.

<table>
<thead>
<tr>
<th>Solute</th>
<th>l.s.f.(δ)</th>
<th>(δ)⁴/³</th>
<th>Equilibrium Conc.</th>
<th>Increase in yield stress</th>
<th>Relative effect</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bi</td>
<td>0.0696</td>
<td>0.0286</td>
<td>1.0%</td>
<td>7.2×10⁻⁴µ</td>
<td>8.2</td>
</tr>
<tr>
<td>Cd</td>
<td>0.0520</td>
<td>0.0194</td>
<td>0.75%</td>
<td>3.6×10⁻⁴µ</td>
<td>4.1</td>
</tr>
<tr>
<td>Hg</td>
<td>0.0620</td>
<td>0.0245</td>
<td>1.0%</td>
<td>6.1×10⁻⁴µ</td>
<td>6.9</td>
</tr>
<tr>
<td>In</td>
<td>0.0106</td>
<td>0.0023</td>
<td>6.5%</td>
<td>3.7×10⁻⁴µ</td>
<td>4.2</td>
</tr>
<tr>
<td>Pb</td>
<td>0.0887</td>
<td>0.0396</td>
<td>2.5%*</td>
<td>25×10⁻⁴µ</td>
<td>28</td>
</tr>
<tr>
<td>Sb</td>
<td>0.0179</td>
<td>0.0047</td>
<td>0.75%</td>
<td>8.8×10⁻⁴µ</td>
<td>1</td>
</tr>
<tr>
<td>Zn</td>
<td>0.0194</td>
<td>0.0052</td>
<td>0.2%</td>
<td>2.6×10⁻⁴µ</td>
<td>0.30</td>
</tr>
</tbody>
</table>

* at 183°C

Table 36 Predicted Effect of Various Solutes on the Solid Solution Strengthening of Tin.

The data above is restricted to those solutes for which the linear size factors have been determined with a reasonable degree of accuracy, and values of equilibrium solubility are the best estimates available in the literature. It should be noted that that solubility data is not available for lead at room temperature, and the values for cadmium and mercury are open to some doubt. The increase and relative effect columns give the effect on the yield stress, and the relative strengthening efficiency by saturating tin with each of the elements, taking antimony as the reference solute.
Table 36 suggests that large benefits should be obtained by substituting Bi, Cd, Hg, In or Pb in place of antimony in tin based alloys to obtain a greater degree of solid solution strengthening. In practice this expectation is not realised, and increases are much less than that predicted.

<table>
<thead>
<tr>
<th>% Solute (wt)</th>
<th>Bi</th>
<th>Cd</th>
<th>Pb</th>
<th>Sb</th>
<th>Zn</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>7.5</td>
<td>5</td>
<td>5</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>0.1</td>
<td>8.3</td>
<td>9</td>
<td>9</td>
<td>9</td>
<td>9</td>
</tr>
<tr>
<td>0.5</td>
<td>11.1</td>
<td>13</td>
<td>13</td>
<td>13</td>
<td>13</td>
</tr>
<tr>
<td>1.0</td>
<td>11</td>
<td>14.7</td>
<td>14</td>
<td>14</td>
<td>14</td>
</tr>
<tr>
<td>2.0</td>
<td>13</td>
<td>17.4</td>
<td>15</td>
<td>15</td>
<td>15</td>
</tr>
<tr>
<td>5.0</td>
<td>18.5</td>
<td>13</td>
<td>13</td>
<td>13</td>
<td>13</td>
</tr>
</tbody>
</table>

Test method  
A = Brinell test \( L/D^2 = 5 \), 30 sec. indentation
B = Brinell test Conditions unspecified
C = Vickers test 2.5Kg load, 30 sec indentation
D = Brinell test \( L/D^2 = 2.5 \), 30 sec indentation

Table 37 Hardness of alloys vs composition

Data on the mechanical properties of solid solutions and dilute 2 phase alloys are shown in table 37 above. Information on mechanical properties is scarce, particularly at very low solute concentrations, and the above data is extracted from Greenfield and Forrester\(^{(38)}\) for reasonably consistent testing conditions.
Although hardness improvements are found over tin-antimony alloys of the same concentration, these do not correlate well with the predicted magnitude of strengthening. In particular zinc would be expected to show a very small effect on the properties, but in practice it is shown to strengthen just as effectively as cadmium. The anomalous behaviour of zinc can be understood to some degree by considering the electronic interactions between zinc and tin. In many solid solutions the atomic volume of the solute in the lattice of the solvent (fl*B) is similar to its atomic volume in its own (solute) lattice (ΩB). This implies that the electronic environment of the solute is only slightly modified by the solvent. In the case of zinc Ω*B is much larger than ΩB indicating that the electronic environment of the zinc atom is extensively modified by the tin lattice. This might be expected from a change in electron:atom ratio by dissolving divalent zinc in tin which normally has a valence of 4, but can not be quantified in these terms since cadmium is also divalent, yet the change in Ω*B is only about one tenth that found in zinc. Unfortunately no direct use can be made of these values since a relationship that incorporates the effects of both atomic size and electronic factors has not yet been established.
Since tin based alloys with potentially useful properties cannot be identified from fundamental considerations, the selection of alloys for further study has been made on an empirical basis.

The basis addition to tin for all this series of alloys was 0.3% Nickel which has been shown to give the largest increase in hardness at very small concentrations\(^{(38)}\). The hardness deformation curve for this alloy is shown in figure 13, and the \(\log \sigma / \log \varepsilon\) plot in figure 30. Although the hardness is quite low (12 H.V) this is maintained up to 70% deformation. At 90% deformation the strain rate sensitivity is low with no evidence of grain boundary sliding.

To this alloy was added 1% Bismuth, which is the equilibrium solubility at room temperature, to add further solid solution strengthening. This resulted in a much harder alloy that showed only a slight tendency to soften on rolling. At 90% deformation the hardness was 15.2 HV with a very similar \(\log \sigma / \log \varepsilon\) plot to the Sn/0.3% Ni alloy, except that it was displaced to higher stresses. The low values of the S.R.S. in these two alloys is also consistent with the grain size of 30\(\mu m\), which is too coarse to permit significant sliding. The only remaining element with any significant solubility in tin was Antimony. This was added at the 2% level since in Sn/Sb alloys a 2% addition gave only a small volume fraction of SbSn. A further increase in hardness in the 90% deformed condition was obtained (16.9 HV) over the previous alloy, and this was only 0.5 HV less than
the hardness of Sn/6% Sb/2½% Cu in the same condition, but with a much lower softening tendency. The strain rate sensitivity was higher in the Sn/Ni/Bi/ Sb alloy and the creep properties inferior to the antimony free composition, presumably due to a finer grain size, although it was not possible to verify this as grain boundary delineation could not be obtained by etching in this alloy. Evidently the solubility of antimony in tin is also reduced in these quaternary alloys to below 2% at the solidus, as some of the SbSn was present as very small cuboids suggesting that it had been formed from the melt. In tin antimony binary alloys cuboids are not observed until 9% Sb where they are formed as the first solid to crystallise. Figure 33 shows the Sn/0.3% Ni/ 1% Bi/2% Sb alloy to have slightly better properties than the commercial 6% Sb pewters at all strain rates. This is contradictory to its slightly lower hardness, and it must be assumed that the two hardness values lie within each others error bars which amount to approximately ±1 HV.

Further efforts to improve rolled hardness by decreasing the antimony level to 1% and adding 0.5% zinc were unsuccessful due to an increased tendency to soften on deformation, but a higher cast hardness of 21.3 HV was obtained. Zinc additions were made with reference to the encouraging results of Mykura (74) with high zinc content alloys, but the amount was reduced to minimise the quantity of zinc oxide formed in melting.
Of all the new alloys examined that based on the composition Sn/0.3% Ni/1% Bi/2% Sb was the most successful. This composition had properties comparable with existing commercial compositions but with the advantage of a lower softening rate which would result in a higher strength where further appreciable deformation is introduced in the fabrication process (i.e. spinning). Against this must be set the higher production costs involved in the manufacture of low melting point master alloys and the higher tin content. In this last respect pewter production is unusual as the cost of tin is higher than the cost of most alloying additions, and hence the more highly alloyed compositions contain a lower metal cost content than the pure metal itself.
Cast binary pewter is essentially a supersaturated solution of antimony in tin. The amount of the intermetallic phase SbSn is very small and is mainly confined to a discontinuous grain boundary precipitate. Pewter alloys containing copper have the additional phase Cu₆Sn₅ present both as needles of the primary intermetallic, and as a dotted eutectic. When pewter is deformed by rolling at room temperature changes occur in the mechanical properties in two distinct stages. At low deformations (< 25%) the material is hardened by conventional strain hardening. Larger deformations result in a softening of the material from this maximum value, and are accompanied by recrystallisation of the matrix and extensive precipitation of SbSn. In this condition the grain size may be mixed if the alloys are not homogenised, but contain a large proportion of very fine grains (<10 microns).

In general the loss of hardness, the amount of precipitate and the recrystallised grain size are all influenced by the amount of deformation, large deformations producing a large loss in hardness, a higher volume fraction of SbSn and a smaller grain size. In binary alloys containing only 2% antimony these effects are hardly noticable, but ternary alloys and binary alloys containing larger antimony additions show increased amounts of softening as the proportions of
alloying additions are increased. When rolled pewter is heated partial or complete resolution of the SbSn precipitate occurs depending on the temperature and alloy composition. This is accompanied by an increase in grain size. At low temperatures where there is no resolution of the precipitates grain growth occurs by the boundaries breaking free of their pinning points, whilst at high temperatures above the $\alpha/\alpha + \beta$ boundary unimpeded grain growth may result in a final grain size of many millimeters. In this condition the hardness is similar to that of the cast ingot, although lesser hardness increases are obtained at lower temperatures.

Although reference is frequently made to the results of Vickers hardness tests these are not always informative with these alloys since they are composed of the combined effects of a high strain rate indentation followed by a period of creep at low strain rate. Tests at a variety of strain rates have shown that alloys with a similar Vickers hardness may behave very differently at low and high strain rates.

The poor mechanical properties of rolled pewter sheet when measured in a slow tensile test are due to a loss of solid solution strengthening caused by the precipitation of SbSn and the consequent reduction is grain size. With a sufficiently fine grain size and a test temperature in the creep range significant contributions to the testing strain can be made by grain boundary sliding. Since this process
requires a lower applied stress than is needed for slip a lower flow stress is observed. The high values of strain rate sensitivity, fairly large ductilities, and the low values of the activation energies for creep measured at low strain rates all demonstrate that superplastic flow occurs in rolled pewter and contributes to the low hardness. Whilst this is a most important factor in the softening of pewter only a proportion of the total deformation can be achieved by this route, the remainder being due to slip/dislocation climb where the amount of solid solution strengthening is important. This is particularly true of rolled pewter since the SbSn particles straddle the grain boundaries and reduce the ease of sliding. In cast or solution treated pewter the grain size is too large for grain boundary sliding to contribute to the deformation in the range of strain rates studied. Under these conditions the larger amount of solid solution strengthening predominates and the cast material has a higher flow stress than the same material after rolling.

At high testing speeds boundary sliding cannot contribute in any material condition since the stress required to move the boundaries at a sufficient rate would be greater than that required to cause deformation by slip alone. A consequence of this is that rolled pewter is stronger at high strain rates than cast pewter as its fine grain size is now advantageous in promoting grain boundary strengthening as predicted by the Petch relationship, this being sufficient
to overcome the effects of the loss of solid solution strengthening.

The high cast hardness of alloys containing copper and their high softening rates are not completely understood, but the former appears to be connected with the interstitial nature of copper atoms dissolved in tin which may yield a greater strengthening effect than an equivalent substitutional atom, and the latter to be due the additional amount of Cu₆Sn₅ available for grain refinement.

The solution treatment of rolled pewter gives alloys of enhanced creep resistance with very low values of the strain rate sensitivity factor (<0.1) and correspondingly large values of the stress exponent (n = 11 - 18). The mechanism by which these values are obtained is uncertain. Whilst the n values are certainly very high they are not unique and are comparable to those found in dispersion alloys. The increase in stress exponent shown by age hardening alloys provides an attractive explanation since these pewter alloys have a supersaturated matrix where precipitation is possible, but significant precipitation at very low strains is inconsistent with the results of X-ray diffraction.

Since the softening of pewter when subjected to cold rolling is due to the inescapable breakdown of the solid solution to give a dispersed precipitate with the consequent loss of
solid solution strengthening and very fine recrystallised grain size it follows that any changes to the alloy composition to obtain improved properties should aim at avoiding these phenomena. Work has been directed toward the investigation of systems showing the maximum amount of solid solution strengthening with a controlled amount of second phase precipitate to refine the grain size sufficiently to obtain a useful measure of grain boundary strengthening at high strain rate, whilst not being so fine as to greatly increase the creep rate due to superplastic flow.

The very low solubility of most alloying elements in tin have frustrated this line of development to a large extent, whilst the toxic nature of elements such as cadmium and lead provide further constraints on alloy compositions for pewterware intended for food use. The range of alloys investigated containing nickel, bismuth, antimony and zinc show interesting properties with decreased softening rates, but none have a rolled hardness significantly higher than that obtained with conventional compositions over the range of deformations studied. Much greater improvements in hardness have been obtained from tin/6% Zn/1-2% Sb alloys prepared by Mykura\(^{(74)}\) which also show low softening rates. There has, however, been some reluctance by commercial producers to investigate this alloy more fully due to the film of zinc oxide formed on the melt and the rather white
colour obtained which is considered to detract from its appearance.

Where the highest hardness is to be obtained from conventional pewter compositions heat treatment still affords the best solution. This is particularly true with shallow pressings where the relatively small deformations produced in fabrication can further strain harden a solution treated blank.

With spun articles the problem is greater since a heat treated blank would be severely softened by the large deformations involved, whilst heat treatment at high temperature in the semi-fabricated condition could lead to distortion by excessive creep in the furnace unless adequately jigged. Where creep properties are at a premium, however, a prolonged low temperature treatment can be beneficial.
7. Conclusions.

1. Cast binary pewter is a metastable solid solution of antimony in tin.

2. When cast pewter is deformed by rolling at room temperature the changes in mechanical properties occur in two stages. (a) At low deformations (<25%) by conventional strain hardening, and (b) when the deformation is increased above 25% softening is observed. The amount of SbSn precipitation increases, and the antimony remaining in solid solution decreases to ≈ 2%. The matrix is partly or completely recrystallised, and the grain size decreases to ≈ 10 μm. or less depending on the exact composition.

3. By solution treatment hardness values similar to the cast hardness are obtained. In this condition enhanced creep resistance is observed, with values for the stress exponent in the range 11-18. The reasons for these high values are not well understood.

4. Vickers or Brinell hardness tests may be misleading in these alloys which show significant creep during testing.

5. The hardnesses of copper bearing alloys are anomalous considering the small solubility of copper in tin. It is thought that this is due to the probable interstitial nature of the copper atom in the tin lattice.

6. Alloys have been produced with controlled amounts of second phase, which have the predicted low softening
rates. With the exception of alloys containing 6% Zn. and 1-2% Cu. they do not have deformed hardnesses significantly different from conventional pewters.

7. The best mechanical properties can be obtained in pewter by solution treatment followed by small amounts of cold work (up to 25%). This could be done before the manufacture of shallow pressings, or for more limited applications, by spinning solution treated blanks where the total deformation is not too large.
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PLATE 1
6\% Antimony Pewter (as cast)  Nital etch  X35

PLATE 2
6\% Antimony Pewter  Rolled 10\%  Nital etch  X35
PLATE 3

6% Antimony Pewter  Rolled 90% Nital etch  X400

PLATE 4

6% Antimony, 2% Copper Pewter (as cast) Nital etch X35
PLATE 5

6% Antimony, 2% Copper Pewter. Rolled 20% Nital etch X600

PLATE 6

6% Antimony, 2% Copper Pewter, Rolled 90% Nital etch X600
PLATE 7
4% Antimony Pewter, Rolled 30%. Nital etch + Gold coating
S.E.M. image X900

PLATE 8
4% Antimony Pewter, Rolled 30%, showing an SbSn precipitate on a slip band. Nital etch + Gold coating S.E.M. X10,000
PLATE 9

4% Antimony Pewter, Rolled 30%, showing an SbSn precipitate straddling a high angle boundary. Nital etch + Gold coat S.E.M. image X2,200

PLATE 10

4% Antimony Pewter, Rolled 90%. Electrolytic etch S.E.M. image X4,000
6% Sb. Pewter, Rolled 10% and Argon Ion Etched. Optical micrograph X35, showing small recrystallised grains and a fine dispersion of SbSn produced in preparation.

4% Sb. Pewter. T.E.M. Micrograph. Foil solution treated at 210°C and mechanically thinned by etching and polishing. X 105,000
PLATE 13

6% Antimony Pewter, Rolled 20%. T.E.M. Micrograph of Extraction Replica. X 100,000.

PLATE 13a

Electron Diffraction Pattern from above.
PLATE 14

6% Antimony Pewter, Rolled 20%. T.E.M. Micrograph of Extraction Replica. X 54,000

PLATE 14a

Electron Diffraction Pattern from above.
PLATE 15

6% Sb. Pewter, Rolled 90%. T.E.M. Micrograph of Extraction Replica. X 80,000

PLATE 15a

Selected area diffraction pattern from above.
6% Sb. Pewter, Rolled 90%. T.E.M. Micrograph of Extraction Replica X 80,000

PLATE 16a

Selected Area Diffraction Pattern from above.
PLATE 17
4% Sb. Pewter, Rolled 90%. Heated to 110°C @ 10°C/min. and rapidly cooled. Nital etch. X 360

PLATE 18
4% Sb. Pewter, Rolled 90%. Heated to 170°C @ 10°C/min. and rapidly cooled. X 360
PLATE 19

4% Sb. Pewter, Rolled 90%. Heated to 225°C @ 10°C/min. and rapidly cooled. Nital etch. X 360

PLATE 20

S.E.M. Micrograph of 6% Sb. alloy deformed 30% in uniaxial tension at a strain rate of 1.25x10^{-3}/min. Fiducial scratches show rotation and offsets at the grain boundaries. Unetched. X 15,000
PLATE 21

6% Sb. alloy strained to failure at a rate of $1.25 \times 10^{-3}$ per min. Unetched. Optical Micrograph.

PLATE 22

6% Sb, 2.5% Cu alloy tested under the same conditions as above. Unetched. Optical Micrograph.
$\varepsilon = 1.25 \times 10^{-3}/\text{min.}$
X25 approx.

$\varepsilon = 12.5/\text{min.}$
X25 approx.

$\varepsilon = 1.25 \times 10^{-2}/\text{min.}$
X200 approx.

6% Sb. Alloy, Rolled 90%, Tensile Tested at 20°C
Deep void in the fracture surface of a 6% Sb. alloy showing intergranular decohesion. Rolled 90\%, Tested at 20^\circ C \dot{\epsilon} = 1.25 \times 10^{-3}/\text{min}.

Smooth sided void in the fracture surface of a 6% Sb. alloy Rolled 90\%, Tested at 20^\circ C, \dot{\epsilon} = 12.5/\text{min}.
Tensile test specimens. Tested at $-40^\circ C$ X30 approx.

All 6% Sb. Alloys Rolled 90% before testing.
6% Sb. Alloys, Rolled 90%, Tested at -40°C
Fracture Surface. Tested at 20°C. 6% Sb. Alloy Previously Rolled 90% + 10 Days at 80°C.

Detail from Plate 37 showing smooth sided voids
6% Sb. Alloy, Rolled 90% + 1 Hour at 210°C, Tested at 20°C

\[ \dot{\varepsilon} = 1.25 \times 10^{-3} \text{/min}. \]
## APPENDIX I

<table>
<thead>
<tr>
<th>ALLOY</th>
<th>Sn</th>
<th>Sb</th>
<th>Cu</th>
<th>Pb</th>
<th>Zn</th>
<th>Fe</th>
<th>As</th>
<th>Ni</th>
<th>Bi</th>
<th>Cd</th>
<th>Ag</th>
<th>Al</th>
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</thead>
<tbody>
<tr>
<td>Pure Tin</td>
<td>Bal</td>
<td>0.02</td>
<td>&lt;0.001</td>
<td>0.06</td>
<td>&lt;0.001</td>
<td>0.002</td>
<td>0.002</td>
<td>&lt;0.001</td>
<td>&lt;0.001</td>
<td>&lt;0.001</td>
<td>&lt;0.001</td>
<td></td>
</tr>
<tr>
<td>2% Cu</td>
<td>Bal</td>
<td>0.02</td>
<td>1.7</td>
<td>0.05</td>
<td>&lt;0.001</td>
<td>0.004</td>
<td>0.002</td>
<td>&lt;0.001</td>
<td>&lt;0.001</td>
<td>&lt;0.001</td>
<td>&lt;0.001</td>
<td>&lt;0.001</td>
</tr>
<tr>
<td>4% Sb</td>
<td>Bal</td>
<td>4.0</td>
<td>&lt;0.01</td>
<td>0.14</td>
<td>&lt;0.001</td>
<td>0.005</td>
<td>0.02</td>
<td>&lt;0.001</td>
<td>&lt;0.001</td>
<td>&lt;0.001</td>
<td>&lt;0.001</td>
<td>&lt;0.001</td>
</tr>
<tr>
<td>6% Sb</td>
<td>Bal</td>
<td>5.9</td>
<td>&lt;0.01</td>
<td>0.18</td>
<td>&lt;0.001</td>
<td>0.005</td>
<td>0.03</td>
<td>&lt;0.001</td>
<td>&lt;0.001</td>
<td>&lt;0.001</td>
<td>&lt;0.001</td>
<td>&lt;0.001</td>
</tr>
<tr>
<td>4% Sb 2% Cu</td>
<td>Bal</td>
<td>3.9</td>
<td>2.4</td>
<td>0.14</td>
<td>&lt;0.001</td>
<td>0.006</td>
<td>0.02</td>
<td>&lt;0.001</td>
<td>&lt;0.001</td>
<td>&lt;0.001</td>
<td>&lt;0.001</td>
<td>&lt;0.001</td>
</tr>
<tr>
<td>6% Sb 2% Cu</td>
<td>Bal</td>
<td>6.0</td>
<td>2.5</td>
<td>0.18</td>
<td>&lt;0.001</td>
<td>0.006</td>
<td>0.04</td>
<td>0.001</td>
<td>0.004</td>
<td>0.002</td>
<td>&lt;0.001</td>
<td>&lt;0.001</td>
</tr>
<tr>
<td>6% Sb 2% Cu (Hoyt)</td>
<td>Bal</td>
<td>5.6</td>
<td>1.8</td>
<td>0.05</td>
<td>&lt;0.001</td>
<td>0.004</td>
<td>0.003</td>
<td>0.002</td>
<td>&lt;0.001</td>
<td>&lt;0.001</td>
<td>&lt;0.001</td>
<td>&lt;0.001</td>
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</tbody>
</table>
Appendix II - Chemical Etches

1. **NITAL (1 and 5%)**

   Darkens grains leaving SnSb and Cu₆Sn₅ white and pale straw respectively. Good results obtained with polarised light microscopy. Best retention of detail at 5% concentration, but etching time very short (1 sec.) 1% Nital is more controllable with an etching time of approx. 15 secs.

2. **ALCOHOLIC FERRIC CHLORIDE**

   Effect similar to Nital, but more aggressive. Mildest etch capable of stripping carbon replicas from Pewter substrate. In diluted form can give rather patchy etching.

3. **ACIDIFIED SODIUM SULPHITE**

   Etches grains pale grey in 5 minutes. SbSn and Cu₆Sn₅ remain unattacked. Poor grain contrast.
Appendix III  Electropolishes

1. PERCHLORIC ACID ETCH

15% Perchloric Acid (conc.)
10% 2-Butoxy ethanol
75% Ethanol or I.M.S.

Recommended Conditions

12 - 15 volts, 0 - 15°C, stir.

Comments - Black oxide film easily removed. Best results when fresh and at 0°C.

2. PERCHLORIC ACID / ACETIC ANHYDRIDE

20% Perchloric Acid
80% Acetic Anhydride

Recommended Conditions

25 - 40 volts, 15 - 22°C

Comments - Adherent oxide film, Very hazardous to prepare.

3. PERCHLORIC ACID / ACETIC ACID

28% Perchloric Acid
72% Glacial Acetic Acid

Recommended Conditions

Current density 3 - 6 A/dm². No temperature quoted.

Comments - Adherent oxide film, Very high conductivity.

4. HYDROCHLORIC ACID

10% Hydrochloric Acid (conc)
90% Water

Recommended Conditions

Current density - very low, No temperature quoted.

Comments - Grey pitted surface.
5  ACID SULPHATE PLATING BATH

40 gms./litre Tin, as Stannous Sulphate
50 gms./litre Sulphuric Acid
40 gms./litre Cresolsulphonic Acid
2 gms./litre Gelatin
1 gm./litre B-naphthol 1

Recommended Conditions

0.4 (minimum) - 1.5 volts, 20°C, 10 A/sq. foot in still bath, 100 A/sq. ft. with agitation.

Comments - Severe pitting at all voltages, current densities and temperatures. Surface is clean and free from oxide.

6  STANNOUS FLUOBORATE PLATING BATH

80 gms./litre tin, as Stannous Fluoborate
150 gms./litre Fluoboric Acid
6 gms./litre Gelatin
1 gm./litre B-naphthol 1

Recommended Conditions

1 - 3 volts, 16 - 38°C. Still bath 20 - 120 A/sq. ft.

Comments - Adherent oxide film.
Appendix IV

Deconvolution Program for use with E.D.S. data from Electron Probe Microanalysis

C-PS8 FOCAL, 1971

01.01 L S DTA0:EPMA
01.02 T "NUMBER OF CHANNELS MUST BE LESS THAN 160" !
01.03 T "AND MUST BE AN INTEGER TIMES 10" !
01.04 A "HOW MANY CHANNELS? " N
01.05 A "IS THIS ON FILE? " A;I (A-YES)1,06,1,13,1,06
01.06 T "LOAD DATA TAPE FROM THE BEGINNING OF THE FIRST CHANNEL IDENTITY"!
01.07 T "TO THE END OF THE LAST CHANNEL (+ FINAL CARR. RETURN) !
01.08 F A=1, (6*N/5); A I(A)
01.09 T ! ;T "THANK YOU" !;O O DTA0:PROBE.FD
01.10 F J=12,12, (6*N/5); F X=(J-10),1,(J-1); T %6.ØØ, I(X) !
01.11 O C
01.12 C FILE NOW ON MAG TAPE
01.13 O I DTA0:PROBE.FD
01.14 F X=1,1,N; A I(X)
01.15 O I TTY:,E ;T !!! ;  T "SAMPLE................" !!!
01.16 A "SPECTRUM START ENERGY (EV)? " EO
01.17 A "START INTEGRATION AT (EV)? " EL
01.18 A "ENERGY STEP/CHANNEL (EV)? " DE
01.19 A "FINISH AT (EV)? " EU
01.20 A "MEAN ENERGY OF FIRST PEAK (EV)? " E1
01.21 A "MEAN ENERGY OF SECOND PEAK (EV)? " E2
01.22 S UC=(EU-EO)/DE; S LC=(EL-EO)/DE
01.23 S F=(I(UC)-I(LC)); S A=I(LC)
01.24 A "INTEGRATED INTENSITY OF FIRST PEAK? " EL
01.25 A "INTEGRATED INTENSITY OF SECOND PEAK? " EU
01.26 F X=LC, 1,UC; D 4

02.01 S T=Ø; S S=Ø
02.02 F X=LC,1,UC; D 3
02.03 S S=S/T
02.04 S A=((E2-S)*EU)/(S-E1)*EL)
02.05 S A=100/(A+1); T !!
02.06 T "MEAN ENERGY IS " %9.Ø4, S !
02.07 T "PERCENTAGE OF SECOND PEAK IS " %5.Ø2, A !!!
02.08 T "INTEGRATED INTENSITY IS " %7.Ø4, T !!!
02.09 G 1.Ø4

03.01 S T=T+I(X)
03.02 S S=S+(I(X)*((X*DE )+EO))

04.01 S I(X)=I(X)-(A+(P*(X-LC)))

05.01 QUIT