A STUDY
ON
THE RECRYSTALLIZATION CHARACTERISTICS
OF HIGH PURITY LEAD AND ITS ALLOYS

A THESIS
SUBMITTED TO THE FACULTY OF THE UNIVERSITY OF NEVADA
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INTRODUCTION

When a cold worked metal is heated, the distorted metal tends to revert to its pre-worked condition. The driving force is the extra energy of the defects, such as vacancies and dislocations, introduced by cold working. The change to the pre-worked condition, that is, recrystallization, occurs through a rearrangement of the atoms of the metal into a new set of grains.

Though metals have been worked and annealed since remote times, interpretation of these processes dates from 1881 when Kalisher\(^{(1)}\) attempted to explain changes in the "molecular structure" of cold worked zinc during heating. Since then, there have been numerous studies of recrystallization which have been summarized in a number of articles.\(^{(2 - 8)}\)

Lead is one of the oldest metals known to man. The earliest known specimen dating back to about 3,000 B. C. was found in "the Temple of Osiris at Abydos" and is preserved in the British Museum.\(^{(9)}\) One of the most interesting historical applications of the metal was its general use by the Roman people for water pipes. This early application of the lead is probably due to the availability of its oxidized ores on the surface of the earth, and its easy reducibility. Its use probably arises from its low melting point, softness, ductility,
low chemical reactivity with atmospheric gases and its resistance to weathering and to certain chemicals including hard water.

Metals, when pure, recrystallize at about one third of the absolute melting point, which for lead is below 0°C. While it is well known that certain impurities raise this recrystallization temperature, no systematic study has been attempted. Thus many of the early studies on relatively impure lead are of limited value.

In this investigation, the minimum strain necessary for the room temperature recrystallization of 99.9997% purity lead was determined. The effect of additions of selected alloying elements on recrystallization was then examined.
REVIEW OF PREVIOUS WORK

General

When a metal is cold worked, most of the mechanical energy expended is converted into heat, but a small fraction is absorbed by the metal. Because of this excess energy, a cold worked metal is not stable and tends to revert to a strain-free state when annealed, through recrystallization.

The annealing process is composed of three stages; recovery, recrystallization, and grain growth. Though polygonization is sometimes viewed as an intermittent between recovery and recrystallization, it is treated here as a part of recovery. Since the annealing process involves some form of atoms, or vacancy, movement as well as dislocation movement, it is an extremely temperature sensitive process.

The present understanding of recrystallization is unsatisfactory. The two dominant theories, grain boundary migration and nucleation and growth, are reviewed later.

Nature of Cold Worked Metal

The internal strain energy stored in the metal during cold work is associated with various defects created by the deformation. The amount of energy retained, therefore, depends on a number of variables such as the deformation process, deformation temperature and composition of the
metal. This amount of internal energy is usually increased by lowering the deformation temperature, increasing the severity of the deformation, and by alloying. Thus the stored energy of high purity copper is only 6 cal/mole after 30 per cent extension at room temperature, \(10\) while that of a 82.6\% Au - 17.4\% Ag alloy drilled at the temperature of liquid N\(_2\) is 200 cal/mole. \(11\)

The energy may be stored in a number of ways.

1. Elastic energy: This is usually a very small fraction of the total stored energy.

2. Energy due to generation and redistribution of dislocations: The density of dislocations is increased from \(10^6 - 10^8/cm^2\) for annealed metals to about \(10^{11} - 10^{12}/cm^2\) after heavy deformation. \(12\) The distribution and energy of the dislocations are also altered by the cold work.

3. Energy due to creation of vacancies and, in some instances, interstitials: The number of vacancies in a crystal at equilibrium is a function of their molar energy of formation and varies exponentially with temperature. The number of vacancies created by cold work has been estimated indirectly (usually based on the known effect of vacancies on some properties which were altered by the cold work).

4. Energy due to the formation of stacking faults, twinning, and the destruction of order in the case of
Cold work produces structural changes in the metal. On deforming, slip lines first appear in grains where the slip planes are favorably oriented for yielding, and in some metals, such as zinc, twin bands also appear. As the degree of deformation increases, slip lines appear in an increasing number of grains, the grains tend to rotate, the crystal planes become curved, and the grains become sensibly elongated in the direction of flow. Since the directions in the crystal grains by which flow can take place during deformation are determined by crystal symmetry, preferred orientation results. This preferred orientation depends on the nature of the deformation process and on the crystal structure of the metal. The increase in the number of defects during deformation is accompanied by an increase in strength, hardness, electro-potential, thermal expansion coefficient, compressibility, and general tendency to corrode, and by a decrease of ductility and electrical conductivity.

Recovery

This can be defined as a process whereby a cold worked metal recovers some of its original physical and mechanical properties without any apparent structural change. However, in the metals which soften before
recrystallization takes place, changes which consist of a reduction in dislocation density and of polygonization have been observed in the temperature range of traditional recovery.\(^{(13,14)}\) The process of recovery is usually studied by measuring the release of the stored energy which occurs through; -

1. Mutual annihilation of dislocations of opposite sign.
2. Shrinkage of dislocation loops until they disappear.
3. The absorption of dislocations by the crystal boundaries that move through the deformed metal.
4. Redistribution of line defects into a more stable array.
5. Reduction in the total area of crystal boundaries.
6. Decrease of surface free energy by a change of shape or orientation.

The time required to recover a given fraction of the total yield recovery, \(\gamma\), is given by an Arrhenius equation of the form

\[
\frac{1}{\gamma} = Ae^{-Q/RT}
\]

where

- \(A\) = Constant
- \(Q\) = Activation energy
- \(R\) = Gas constant
- \(T\) = Absolute temperature
Recrystallization

Recrystallization is basically different from recovery. In an isothermal anneal, recrystallization starts slowly, builds up to a maximum reaction rate and then finishes slowly, while the rate of a recovery process always decreases with time.

There are currently two distinct theories of recrystallization, a grain boundary migration theory and a nucleation and growth theory.

a) Grain Boundary Migration

This theory was proposed by Beck and Sperry\(^{15}\) in 1950 and supported recently by Bailey and Hirsch.\(^{16}\) The latter observed, by electron microscopy, that after small to moderate amounts of deformation, recrystallization occurred by the migration of the original grain boundaries. Their conclusion was deduced from the fact that the activation energy for recrystallization was that for boundary migration.

In this theory, recrystallization occurs by the migration of a grain boundary in a direction normal to itself. The new grains are believed to be formed by the growth of initially small pieces of the old ones.\(^{17}\) The driving force is the difference in energy between the cold worked and the annealed state of the metal. Though the velocity of boundary movement depends on the driving
force, as Mott has shown, the wide range in the
mobilities of different grain boundaries is largely due
to differences in orientation.

For convenience, grain boundaries are classified
as follows:

1) The small angle ($\theta < 1^\circ$) simple Burgers boundary,
containing one family of parallel and uncontracted edge
dislocations. This type of boundary is of high mobility.

2) The small angle simple Burgers boundary with
a larger change of angle ($5^\circ < \theta < 20^\circ$) and contracted
dislocations. Since, as Dunn and Daniels have shown, the growth of polygonal domains becomes much slower, when
the angle between them increases, this type of boundary is
not very mobile. According to Lomer and Nye, boundaries made from contracted dislocations should be immobile,
because the Peierls-Nabarro force resisting the motion
of a dislocation increases rapidly as the width of the
dislocation is reduced.

3) The small or medium angle unsymmetrical boundary
containing dislocations with more than one kind of Burgers
vectors. This type appears to be immobile and is often
found in worked polycrystals.

4) The larger angle ($\theta \geq 30^\circ$) incoherent boundary
across which there is no continuity along lattice rows.
This is a mobile boundary. A large angle boundary moves
rapidly by the movement of atoms from one crystal to the other, for each atom in such a boundary is next to a defect similar to a vacant atomic site.

The isothermal behavior of recrystallization is explained by the dependence of mobility on orientation. The angle of the boundary of a growing piece is small at first, so is its moving velocity. As the crystal grows, the growing piece advances into more remote regions of the crystal where it makes a large angle boundary, because of the different orientation from its own. Therefore, the boundary velocity is increasing towards a maximum rate.

The fact that crystals deformed in laminar flow do not recrystallize is also explained by this dependence of mobility on orientation, for the orientation in the crystals so deformed does not vary widely enough to allow the formation of a large angle boundary.

A favorable site for the start of recrystallization is the most intensely curved region of the crystal. Since the orientation of this region is so different from average, a grain growing out of this region can quickly make a large angle boundary. On this high energy block hypothesis, a block, once formed, becomes a recrystallization nucleus by a sequence of unit processes, progressively relieving the strain in the block. According to the low energy block hypothesis, the block is considered to be crystallite
that has received much less than the average deformation. In this block hypothesis, the nucleation period is interpreted as a period of relatively slow growth of the block to macroscopic dimensions, or as a period associated with the relief of strain energy within the block. Sometimes there can be dislocation free subcrystals in the specimen after recovery (polygonization) which are apparent nuclei.\(^{(21,22)}\)

b) Nucleation and Growth

This theory views recrystallization as a primary nucleation and growth process. New crystals are nucleated at sites of unusually high energy such as grain boundaries in polycrystalline specimens, and slip, deformation and twin bands in single crystals. In each case it appears that nucleation occurs at points of strong local lattice curvature. However, there has been an alternative suggestion that the real nucleus is in a region of low deformation adjacent to the highly deformed region. Nucleation is believed by some\(^{(23)}\) to be due to the diffusion of atoms under the action of elastic stress gradients. Nuclei are also formed at points of high energy lying in active glide planes.

A different suggestion\(^{(24 - 27)}\) is that polygonization provides the nuclei for recrystallization, small polygonized regions grow that adjoin large angle boundaries. The rate of polygonization is faster, the greater the curvature, or the smaller the radius. Therefore the incubation time for
a nucleus is proportional to the radius of curvature of the boundary.

It is surprising that nucleation should occur at all, for the difference in free energy between a cold worked and an annealed metal is much smaller than that between distinct crystallographic phases. It is probably due to the uneven distribution of the elastic strain in the deformed metal. This unevenness is greater in polycrystalline metals than in a single crystal, because the restraining action of the grain boundary leads to very marked grain distortion in its vicinity. Quite a different idea about recrystallization nuclei is that they form at impurity particles,\(^{(2,8)}\) however there is no experimental proof of this. Even with the many different suggestions and proposals, very little is known about the process of nucleus formation.

Once formed, the nuclei grow until they impinge on each other. This growth is profoundly affected by the local state of internal strain of the deformed lattice. There are some experimental observations on this effect.\(^{(29,30)}\)

Isothermal recrystallization is customarily described in terms of the parameters \(N\), nucleation frequency defined as the number of nuclei formed per second in a cubic centimeter of unrecrystallized matrix, and \(G\), the linear rate of grain growth defined as the rate of change of the diameter.
of a recrystallized grain with time.

Several equations (31,32) have been derived starting with these parameters \( N \) and \( G \) which express the amount of recrystallization as a function of time. On the assumption that diffusion is not required over substantial distances and that the average composition of the reactant does not change with the progress of the reaction, Johnson and Mehl (32) found that the fraction of the volume transformed, \( f(t) \), in time, \( t \), is given by

\[
f(t) = 1 - e^{-\frac{2\pi}{3} N G^3 t^4}
\]

where

\( N = \text{Nucleation frequency} \)

\( G = \text{Growth rate} \)

According to Mehl and his co-workers, (33,34) for a given composition and degree of deformation, \( N \) increases with temperature as follows;

\[
N = A_N e^{-\frac{B_N}{RT}}
\]

where

\( A_N \) and \( B_N \) are constants

\( R \) is the gas constant

The rate of growth, \( G \), is independent of time and
related to the temperature by;

\[ G = A_G e^{-\frac{B_G}{RT}} \]

where \( B_G \) is not a constant, but decreases with increasing temperature and with increasing strain.

The recrystallization rate is given by the equation;

\[ \frac{d\gamma}{dt} = A e^{-\frac{Q_T}{RT}} \]

where \( Q_T \) is the activation energy for recrystallization.

The dimensions of the growing grain are generally described by the relation;

\[ D = G(t - \zeta) \]

where \( \zeta \) is the nucleation period, and the average \( \zeta \) is reciprocally related to the nucleation frequency, \( N \).

**Effect of Variables on Recrystallization**

The main variables which affect the recrystallization behavior are 1) amount of deformation, 2) temperature, 3) time, 4) initial grain size, 5) purity, and 6) amount of recovery prior to the start of recrystallization.
The general relationship of these variables to the recrystallization process is stated in the "recrystallization laws." (4, 5)

1) Amount of Deformation

A minimum amount of deformation (critical strain) is needed to cause recrystallization. The nucleation frequency increases by a much larger factor with an increase in strain than does the growth rate. The growth rate increases as \( \xi^n \) (where \( n > \) unity) for small strains \( (\xi < 5\% - 10\%) \) but is practically independent of strain for larger strains \( (\xi > 15\% - 20\%) \). This growth rate is also dependent on the specific type of deformation as well as on the overall strain. (35)

2) Temperature

The higher the temperature, the shorter the time needed for recrystallization. Generally, the activation energy for nucleation and growth is the same except for small strains \( (< 5\%) \) where \( Q_N > Q_G \).

3) Time

Recrystallization is promoted with an increased period of time, but \( G \) is generally independent of time. During recrystallization, grains grow at a constant rate for a time, and then practically stop growing before impingement. Usually \( N = 0 \) at \( t = 0 \) and \( N \) increases
sharply with increasing time.

4) **Initial Grain Size**

The larger the original grain size, the greater the amount of cold work required to produce an equivalent recrystallization temperature. This is because the grain boundary surface energy is less for larger grains. Since the grain boundaries in the polycrystalline metal act to interrupt the slip processes during cold work, the lattice adjacent to the grain boundaries is more distorted than in the center of the grains. Therefore, the volume and uniformity of the distorted area is increased with a decrease in grain size. This, in turn, increases the number of possible sites for nucleation. However, some deviations from this general rule have been reported.\(^{(34)}\)

5) **Purity**

The presence of impurities in a metal generally retards the recrystallization process. Since impurity atoms in a metal segregate to grain boundaries,\(^{(36)}\) the movement of the grain boundaries is retarded by the necessity for solute atoms to diffuse with them. When a foreign atom migrates to a grain boundary, its elastic field is lowered. The effects of different and specific impurities have been reported.\(^{(37,38)}\)
6) Amount of Prior Recovery

With increasing amounts of recovery the recrystallization temperature also increases, because a larger amount of internal strain is released.

Grain Growth

After the primary recrystallization is complete, grain growth occurs, the driving force being due to the decrease of the surface energy of the grain boundaries with larger grains. The mechanism of grain growth can be explained with a soap cell model. The cell which is concave toward the center is unstable, while the cell which is convex toward the center is stable. The critical number of cell sides is six. Therefore, all cells with less than six sides are unstable and tend to diminish. Actually, however, the number of sides of a cell can be changed during the process in a manner shown in Fig. 1.

![Diagram of grain growth mechanism](image-url)

Fig. 1. A mechanism for changing the number of sides of a grain during grain growth
Fig. 2 shows the elimination of both a four and a three sided cells.

![Diagram of four and three sided cells]

Fig. 2. A mechanism of elimination of four and three sided cells

While this soap cell model is completely applicable to the explanation of grain growth in metals, little is known about the mechanism by which atoms cross the grain boundary. Though the proposal by Harker and Parker (40) is generally accepted, a more adaptable mechanism awaits a more detailed explanation of the structure of metallic grain boundaries.

The relationship between the initial grain size, \( D_0 \), and the grain size after time \( t \), \( D \), is generally given by: \((41)\)

\[
D^2 - D_0^2 = kt
\]

where \( k \) = Constant
Neglecting $D_0$ as being very small compared to $D$,

$$D = kt^n$$

where $n$ is usually $< 0.5$

This value of $n$ has been found not to be constant for a given material, when the isothermal reaction temperature is changed.

Factors affecting grain growth involve temperature, geometry of the sample and the presence of impurities. The effect of temperature is given by the relation;

$$G = Ae^{(Q_\gamma/RT)}$$

where $Q_\gamma = \text{Activation energy for grain growth}$

$A = \text{Constant}$

The geometry of a sample has a significant effect on determining the final grain size, because a free surface stops grain growth normal to the surface.\(^{41, 42}\)

Solute atoms in solid solution at the grain boundaries retard normal surface tension induced motion, because the boundaries have to carry the impurity atmosphere along with them. Insoluble particles tend to anchor the boundaries,
for the strain around such a particle is reduced when it is in a boundary. Solute atoms in the form of second phase impurities also inhibit grain growth, because the grain boundary must pull itself through the impurities which lie in its path.

When inclusions are present, the driving force for grain growth is given by the following equation;

\[ \eta = \frac{2 \gamma}{R} = n_s \pi r \eta \]

where \( \eta \) = Driving force per unit area for grain boundary movement.
\( \gamma \) = Surface tension of the grain boundary
\( R \) = The radius of the curvature of the boundary
\( n_s \) = Number of inclusions per unit area
\( r \) = Radius of the particles

**Recrystallization Texture**

A preferred orientation may result from recrystallization. There are two mechanisms proposed.

1) Oriented nucleation hypothesis

Recrystallization nuclei are supposed to have the preferred orientation from the start. The subcrystals produced by polygonization have the preferred orientation.

2) Recrystallization nuclei may be randomly oriented, however, by the orientation dependence of their
growth rates, only selected nuclei can grow.

Secondary Recrystallization

When grain growth is inhibited as a result of the dispersion of a second phase (inclusion inhibited growth), or the presence of a marked preferred orientation (texture inhibition), a secondary recrystallization is often possible. This secondary recrystallization is the same as primary recrystallization in the sense that there is a nucleation period and then growth. The driving force, however, is the difference of surface energy rather than the difference of strain energy. Nevertheless, slight deformation may decrease the nucleation period. While the cause for nucleation for secondary recrystallization is not clear, there are two suggestions.

1) When the grain growth is inhibited by the preferred orientation, grains slightly larger than average and with high angle boundaries may grow slowly at first but the growing rate can be accelerated as the difference of the size increases.

2) When the grain growth is inhibited by the presence of inclusions, boundaries with smaller inclusion densities may be able to move before others do. This mechanism can be aided by dissolution of inclusions as the temperature increases.

Secondary recrystallization is not controlled by
the growth inhibition factors controlling the grain growth after primary recrystallization such as inclusions and a free surface. The nuclei grow until the matrix is completely recrystallized. The number of grains that finally result depends only on the number of secondary nuclei.

**Recrystallization of Lead**

There have been several studies on the recrystallization of lead which have been summarized by Greenwood. It was found that pure lead recrystallized at room temperature after about 3 per cent deformation. Many of the early works are of limited value through the different purities used. However, some attempts have been made at examining specific impurity effects. Thus Worner found that increasing the amount of silver from 0 to 0.05 per cent had the effect of increasing the percentage of reduction for spontaneous recrystallization of lead progressively from 5 to 40 per cent. It was also reported that additions of small amounts of silver, tellurium, and antimony and cadmium increased the recrystallization temperature markedly, while copper, antimony and nickel did so only slightly. With commercial lead (99.9 - 99.99%), the effects of different amounts of copper, antimony, arsenic, copper and nickel, copper and silver, and copper and tellurium, and the effects of 0.05 weight per cent of bismuth, tellurium, silver, zinc, copper, nickel and calcium have been
examined. Some of effects of alloying elements are shwon in Table 1. Table 2 shows the solid solubility limits of the above elements in lead. Since these leads were not oxygen reduced, the effects are difficult to interpret and no consistent pattern emerges.
TABLE 1

Influence of Added Elements on the Work Hardening and Recrystallization of Lead

<table>
<thead>
<tr>
<th>Alloy Composition</th>
<th>Original B.H.N.</th>
<th>½ Min. after 5% Reduction</th>
<th>7 Days after 5% Reduction</th>
<th>Time for Recrystallization to Start (by Etching)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Pb</td>
<td>Cu</td>
<td>Bi</td>
<td>Sb</td>
</tr>
<tr>
<td>0.05%</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.06%</td>
<td>3.4</td>
<td>3.5</td>
<td>3.4</td>
<td>3.7</td>
</tr>
<tr>
<td>0.06%</td>
<td>3.2</td>
<td>4.6</td>
<td>3.4</td>
<td>5.0</td>
</tr>
<tr>
<td>0.06%</td>
<td>3.1</td>
<td>3.5</td>
<td>3.1</td>
<td>3.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Element</td>
<td>Solid Solubility (in at %)</td>
<td>Temperature (°C)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>---------</td>
<td>---------------------------</td>
<td>-----------------</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ag</td>
<td>0.04</td>
<td>100</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Te</td>
<td>0.0065</td>
<td>300</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sb</td>
<td>5.8</td>
<td>247</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cd</td>
<td>0.7</td>
<td>100</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cu</td>
<td>0.2</td>
<td>327</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ni</td>
<td>0.08</td>
<td>R.T.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>As</td>
<td>0.03</td>
<td>R.T.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tl</td>
<td>20</td>
<td>R.T.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bi</td>
<td>18.9</td>
<td>100</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Zn</td>
<td>0.16</td>
<td>318</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ca</td>
<td>0.05</td>
<td>25</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Because of the low melting point ($327^\circ$C), availability in high purity, comparative chemical inertness, and face centered cubic crystal structure (thus easy deformation), lead is a suitable metal upon which the effects of small amounts of additions on the recrystallization behavior of metals can be studied.

The elements, maximum solid solubility of which in lead exceeds 20 atoms per million, are Li, Na, Mg, K, Ca, Cu, Zn, Ga, As, Se, Ag, Cd, In, Sn, Sb, Te, Ba, Au, Hg, Tl, and Bi.\(^{(43)}\)

The alloying elements were chosen to cover a wide range of solid solubility limits in lead,\(^{(54)}\) using those closest to lead in the periodic table. Since additions of small amounts of alloying elements may have considerable effect on the recrystallization behavior,\(^{(55 - 57)}\) the amounts were selected from 0.025 atomic per cent, which was the smallest amount that could be added with accuracy and confidence to the 45 grams ingots, up to their solid solubility limits as shown in Table 3.

Some of the properties of additions are shown in Table 4.
<table>
<thead>
<tr>
<th>Element</th>
<th>0.001%</th>
<th>0.005%</th>
<th>0.01%</th>
<th>0.1%</th>
</tr>
</thead>
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<tr>
<td>T1</td>
<td></td>
<td></td>
<td>0.02%</td>
<td></td>
</tr>
<tr>
<td>Bi</td>
<td>0.005%</td>
<td>0.025%</td>
<td>0.05%</td>
<td></td>
</tr>
<tr>
<td>Sn</td>
<td>0.003%</td>
<td>0.005%</td>
<td>0.01%</td>
<td></td>
</tr>
<tr>
<td>Sb</td>
<td>0.001%</td>
<td>0.005%</td>
<td>0.01%</td>
<td></td>
</tr>
<tr>
<td>Te</td>
<td></td>
<td></td>
<td>0.02%</td>
<td></td>
</tr>
</tbody>
</table>

**Table 3**

Elements Added and Their Wt %
### TABLE 1

Properties of Lead and Alloying Elements

<table>
<thead>
<tr>
<th>Element</th>
<th>at. No.</th>
<th>at. wt.</th>
<th>m.p. (°C)</th>
<th>Crystal Structure</th>
<th>Approximate Values Found in &quot;Constitution of Binary Alloys&quot;[^1]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pb</td>
<td>82</td>
<td>207.21</td>
<td>327.4</td>
<td>F.C.C.</td>
<td>*Solid Solubility in Lead (at.%)</td>
</tr>
<tr>
<td>Tl</td>
<td>81</td>
<td>204.39</td>
<td>302.0</td>
<td>H.C.P.</td>
<td>&gt;20</td>
</tr>
<tr>
<td>Bi</td>
<td>83</td>
<td>209.00</td>
<td>271.3</td>
<td>Rhombohedral</td>
<td>19.05 at 100°C</td>
</tr>
<tr>
<td>Sn</td>
<td>50</td>
<td>118.70</td>
<td>231.89</td>
<td>B.C. Tetra</td>
<td>3.2 3.4</td>
</tr>
<tr>
<td>Sb</td>
<td>51</td>
<td>121.76</td>
<td>630.5</td>
<td>Rhombohedral</td>
<td>5.8</td>
</tr>
<tr>
<td>Te</td>
<td>52</td>
<td>127.61</td>
<td>452.0</td>
<td>Hexagonal</td>
<td>0.0065</td>
</tr>
</tbody>
</table>

[^1]: Approximate Values Found in "Constitution of Binary Alloys"[^1]
EXPERIMENTAL

Material

The lead was obtained from the American Smelting and Refining Co. Its analysis (Table 5) shows total impurities of less than 3 parts per million. This lead was reduced in hydrogen at 550° - 600°C in order to lower the oxygen content to 0.0005 atomic per cent. (58) The purities of the alloying elements were 99.9995, 99.99, 99.998, 99.99 and 99.5% for thallium, bismuth, tin, antimony and tellurium respectively. The impurity contents of the added elements are thus negligible.

Specimen Preparation

The specimens of pure lead were made by rolling the lead ingot down to 0.07 inches thickness at room temperature and by cutting into the size of 0.5 by 2 inches. They were then annealed for two hours at 100°C in air.

The alloy ingots weighing 45 grams were made by melting the basic materials in a cast iron boat under vacuum. The boat was agitated, when molten, to aid in obtaining homogeneity of the alloys. When cool, they were rolled down to 0.07 inches or 0.1 inches thickness for the different series (see later), with intermediate annealing for 30 minutes at 200°C in air. They were cut into the specimen sizes of 0.5 by 2 inches or 0.5 by 1.5 inches for
different series. A final annealing was given for 30 minutes at 200°C in air to produce a fully softened product of coarse grain size. Before the final annealing, all the specimens were polished in a mixture of glacial acetic acid and hydrogen peroxide. However, the composition of the polishing solution had to be adjusted drop by drop for different alloys. A final light polishing was done after the annealing.

Procedure

Specimen deformation was carried out in a 3 by 5 inches Stanat rolling mill. Dimensions before and after reduction were measured by a micrometer. Extreme care was taken, because of the softness of the lead, to ensure that no extra strain was introduced through bending. This involved carefully sliding the lead specimens from one surface to another without at any time lifting them in the air such that they could bend and creep under their own weight.

Recrystallization was followed by microhardness measurements complemented by optical examinations, as the hardness remains constant until recrystallization. A Tukon Microhardness Tester Model LL was used with a nominal load of 50 grams. Because of friction, it appeared that the actual load was 37.5 grams. The value of hardness throughout this investigation represents the average of six
measurements taken in the same interval of length in the same direction on each specimen. A half-hour period after deformation was selected as the recrystallization time; this was standardized throughout the program.

Three series of experiments were completed.

1) Series A

In order to determine the maximum hardness obtainable on pure lead, a specimen was progressively cold worked by increasing amounts of 0.5 per cent reduction followed by hardness measurements. With another specimen of pure lead, the amount of critical cold work was found by taking the hardness 30 minutes after reduction, then this critical amount was used for Series B and C.

2) Series B

This series consisted of a number of alloys containing different amounts of thallium, bismuth, tin, antimony and tellurium.

After reducing by 2.5 per cent in thickness, which was the optimum amount found in Series A, all the specimens were immediately immersed into liquid nitrogen to prevent any recovery until they were ready for measurement. The cold worked hardness at room temperature and a second value after a period of 30 minutes at the appropriate temperature were taken. Half-hour anneals were done at 10°C intervals from 20°C to 100°C and then at 25°C intervals until recrystallization occurred.

- 30 -
3) **Series C**

This series consisted of two parts: firstly, a number of lead alloys containing from 0.05 to 18 per cent bismuth; secondly, lead alloys with the maximum amounts of thallium, bismuth, tin, antimony and tellurium which were to make solid solutions.

After a specific amount of reduction, hardness measurements were taken immediately and after 30 minutes. This procedure was continued with increasing amounts of deformation until recrystallization.
<table>
<thead>
<tr>
<th>Detected Elements</th>
<th>Amount</th>
<th>None Detected Elements by Standard Spectrographic Methods</th>
<th>None Detected Elements by Standard Spectrographic Methods &amp; Chemical Analysis at Limit of Detection of 0.00005%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Element</td>
<td>Impurity (in PPM)</td>
<td>Mg</td>
<td>Si</td>
</tr>
<tr>
<td>Mg</td>
<td>0.5</td>
<td>Mg</td>
<td>Si</td>
</tr>
<tr>
<td>Si</td>
<td>0.5</td>
<td>Mg</td>
<td>Si</td>
</tr>
<tr>
<td>Fe</td>
<td>1.0</td>
<td>Mg</td>
<td>Si</td>
</tr>
<tr>
<td>Cu</td>
<td>1.0</td>
<td>Mg</td>
<td>Si</td>
</tr>
</tbody>
</table>
RESULTS

1) Series A

On working the pure lead, the hardness increased by 21 per cent with the first 0.5 per cent deformation. Thereafter, the increase in hardness was much less rapid up to a maximum of 40.7 per cent at 6.5 per cent deformation (Fig. 3). For greater amounts of work, recrystallization occurred simultaneously. On leaving at room temperature for half an hour after deformation, samples having greater than 2.5 per cent cold work were found to have recrystallized. This critical amount of cold work was used throughout the Series B and C experiments. Results for this Series A are given in Table 6.

2) Series B

(1) Alloys with thallium

After 2.5 per cent deformation, all the low percentage alloys up to 0.01 per cent thallium recrystallized at room temperature. Further additions of up to 5 per cent thallium raised the recrystallization temperature to 100°C and thereafter there was no further increase. The recrystallization temperatures, and the hardmesses in the annealed, worked, and recrystallized conditions of the Tl-alloys are shown in Table 7. Because of grain refining effects of alloying additions, the hardness of the initial fully annealed metal was obtained after recrystallization, only in the low alloy
samples. The larger the amount of alloying element, the bigger the effect of grain refining, thus the less softening after recrystallization. This sequence of grain size effects is shown in Fig. 4 through Fig. 11 and Table 6. This same grain-size effect was observed throughout this investigation in the other series.

(2) Alloys with bismuth

The recrystallization temperature rose gradually from room temperature on the 0.025\% Bi-alloy to 125°C on the 18\% Bi-alloy. The hardnesses in the annealed, and worked conditions also increased to build up to a maximum on the 18\% Bi-alloy. The hardening effect of bismuth was greater than that of same amount of thallium. These results are summarized in Table 9.

(3) Alloys with tin

The same effect of alloying additions on raising the recrystallization temperature was observed on these alloys. The effect of alloying additions on the hardness in the annealed, and worked conditions and on the recrystallization temperature were almost identical to that of bismuth, as shown in Table 10.

(4) Alloys with antimony

A maximum recrystallization temperature of 150°C was obtained with the highest alloy containing 5 per cent antimony. Though the 0.025\% Sb-alloy recrystallized at
room temperature as did the alloys of the same amount of other elements (except for tellurium), the recrystallization temperatures and hardnesses were higher with the same amount of alloying (Table 11). An appreciable hardening of the alloys was observed only with additions above 1.0 per cent.

(5) Alloys with tellurium

The recrystallization temperature was most sensitive to the alloying element in the tellurium-series. With a 0.001 per cent addition, the recrystallization temperature increased to 80°C as shown in Table 12. Some hardening effects of tellurium on the annealed specimens were observed on alloy above 0.025% Te-alloy which is above the solid solubility limit of the element in lead. However, the percentage increase in hardness was approximately constant on all four alloys containing from 0.025 to 1.0 per cent tellurium, the total hardening being low compared to the other series. After reaching 125°C, the recrystallization temperature did not increase further with increasing amounts of tellurium. Although the solid solubility limit had been exceeded, metallographic examination did not show a second phase.

(6) General

The hardness increased with increasing alloy additions as shown in Fig. 12. The maximum percentage hardness increase was obtained with the 18% Bi-alloy, while the smallest increase was one on the 20% Tl-alloy. The effect of the
alloy additions on hardness was greatest on Te-alloys, becoming less on antimony, tin, bismuth, and thallium in that order (Fig. 12).

A further increase in hardness was achieved with the 2.5 per cent cold work. The maximum hardness increase was 130 per cent on the 18% Bi-alloy. The same percentage hardness increases (60 per cent) were achieved on both the 0.1% Te-alloy and the 20% Tl-alloy. These effects of alloying and cold work are illustrated in Fig. 13.

Fig. 14 shows the effect of alloying additions on recrystallization temperature. This effect was greatest on the Te-alloys. However, a further increase of tellurium above 0.075 per cent did not affect the recrystallization temperature. The maximum recrystallization temperature was found on the 5% Sb-alloy.

3) Series C

(1) Bismuth Series

On working these alloys, the hardnesses increased rapidly with the first 5 per cent deformation, then somewhat slowly to build up to a maximum hardness after about 20 per cent deformation. Thereafter, the hardness remained practically constant. Since the hardnesses of the annealed specimens increased progressively with alloy additions, the hardness also increased with bismuth content for the same amount of cold work. As shown in Fig. 15, the maximum
hardness obtained on this series was 10 VHN on the 18% Bi-alloy, and on the 10% Bi-alloy after 25 per cent and 50 per cent deformation respectively. The 5% Bi-alloy could be cold worked up to 45 per cent deformation without recrystallization, but the maximum hardness was only 7.73 VHN. Table 13 shows the hardness change with cold work on this series.

(2) Maximum Solid Solubility Series

The effect of increasing amounts of cold work on hardness is shown in Table 14 and Fig. 16. The maximum hardness was observed on the 5% Sb-alloy after 25 per cent deformation. These series showed no agreement in the amount of work necessary for recrystallization.
TABLE 6

Hardness Change of Pure Lead with Cold Work

<table>
<thead>
<tr>
<th>Amount of Cold Work(%)</th>
<th>VHN</th>
<th>Hardness Increase(%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>3.95</td>
<td>0</td>
</tr>
<tr>
<td>0.5</td>
<td>4.79</td>
<td>21.3</td>
</tr>
<tr>
<td>1.0</td>
<td>4.92</td>
<td>24.6</td>
</tr>
<tr>
<td>1.5</td>
<td>4.95</td>
<td>25.3</td>
</tr>
<tr>
<td>2.0</td>
<td>4.96</td>
<td>25.6</td>
</tr>
<tr>
<td>2.5</td>
<td>4.99</td>
<td>26.3</td>
</tr>
<tr>
<td>3.0</td>
<td>5.10</td>
<td>29.1</td>
</tr>
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<td>3.5</td>
<td>5.25</td>
<td>32.9</td>
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<td>4.0</td>
<td>5.34</td>
<td>35.2</td>
</tr>
<tr>
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<td>5.37</td>
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</tr>
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<td>38.2</td>
</tr>
<tr>
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<td>5.50</td>
<td>39.2</td>
</tr>
<tr>
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<td>5.53</td>
<td>40.0</td>
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<tr>
<td>6.5</td>
<td>5.56</td>
<td>40.7</td>
</tr>
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<td>Amount of Addition (at.%)</td>
<td>Annealed Condition</td>
<td>Worked Condition</td>
</tr>
<tr>
<td>--------------------------</td>
<td>--------------------</td>
<td>------------------</td>
</tr>
<tr>
<td></td>
<td>d*</td>
<td>VHN#</td>
</tr>
<tr>
<td>0</td>
<td>0.1328</td>
<td>3.95</td>
</tr>
<tr>
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<td>0.1308</td>
<td>4.07</td>
</tr>
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<td>0.05</td>
<td>0.1303</td>
<td>4.10</td>
</tr>
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<td>0.075</td>
<td>0.1295</td>
<td>4.15</td>
</tr>
<tr>
<td>0.1</td>
<td>0.1315</td>
<td>4.02</td>
</tr>
<tr>
<td>1.0</td>
<td>0.1310</td>
<td>4.05</td>
</tr>
<tr>
<td>5</td>
<td>0.1338</td>
<td>3.89</td>
</tr>
<tr>
<td>10</td>
<td>0.1313</td>
<td>4.04</td>
</tr>
<tr>
<td>20</td>
<td>0.1295</td>
<td>4.15</td>
</tr>
</tbody>
</table>

* Average length of indentation in mm.

# Vicker hardness number assuming an effective load of 37.5 grams.
<table>
<thead>
<tr>
<th>Composition (at.%)</th>
<th>Recrystallization Temperature (°C)</th>
<th>Grain Size after Recrystallization (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.025</td>
<td>20</td>
<td>4.0</td>
</tr>
<tr>
<td>0.05</td>
<td>20</td>
<td>3.7</td>
</tr>
<tr>
<td>0.075</td>
<td>20</td>
<td>3.0</td>
</tr>
<tr>
<td>0.1</td>
<td>30</td>
<td>2.3</td>
</tr>
<tr>
<td>1.0</td>
<td>100</td>
<td>0.95</td>
</tr>
<tr>
<td>5</td>
<td>125</td>
<td>0.62</td>
</tr>
<tr>
<td>10</td>
<td>125</td>
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<td>20</td>
<td>125</td>
<td>0.23</td>
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<tr>
<td>Amount of Addition (at.%)</td>
<td>Annealed Condition</td>
<td>Worked Condition</td>
</tr>
<tr>
<td>--------------------------</td>
<td>-------------------</td>
<td>-----------------</td>
</tr>
<tr>
<td></td>
<td>d*</td>
<td>VHN#</td>
</tr>
<tr>
<td>0</td>
<td>0.1328</td>
<td>3.95</td>
</tr>
<tr>
<td>0.025</td>
<td>0.1310</td>
<td>4.05</td>
</tr>
<tr>
<td>0.05</td>
<td>0.1325</td>
<td>3.96</td>
</tr>
<tr>
<td>0.075</td>
<td>0.1310</td>
<td>4.05</td>
</tr>
<tr>
<td>0.1</td>
<td>0.1295</td>
<td>4.15</td>
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<tr>
<td>1.0</td>
<td>0.1325</td>
<td>3.96</td>
</tr>
<tr>
<td>5</td>
<td>0.1213</td>
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</tr>
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<td>0.1122</td>
<td>5.53</td>
</tr>
<tr>
<td>18</td>
<td>0.1000</td>
<td>6.95</td>
</tr>
</tbody>
</table>

* Average length of indentation in \( \text{mm} \)

# Vickers hardness number assuming an effective load of 37.5 grams
<table>
<thead>
<tr>
<th>Amount of Addition (at.%)</th>
<th>Annealed Condition</th>
<th>Worked Condition</th>
<th>Recrystallized Condition</th>
<th>Recrystallization Temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>d*</td>
<td>VHN#</td>
<td></td>
<td></td>
</tr>
<tr>
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<td>0.1328</td>
<td>3.95</td>
<td>0.1181</td>
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<tr>
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<td>0.1327</td>
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<td>0.1200</td>
<td>4.83</td>
</tr>
<tr>
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</tr>
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<td>4.79</td>
<td>0.1017</td>
<td>6.76</td>
</tr>
</tbody>
</table>

* Average length of indentation in mm

# Vickers hardness number assuming an effective load of 37.5 grams
<table>
<thead>
<tr>
<th>Amount of Addition (at.%)</th>
<th>Annealed Condition</th>
<th>Worked Condition</th>
<th>Recrystallized Condition</th>
<th>Recrystallization Temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$d^*$</td>
<td>VHN$^#$</td>
<td>$d^*$</td>
<td>VHN$^#$</td>
</tr>
<tr>
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</tr>
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</tr>
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</tr>
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<td>0.0926</td>
<td>8.10</td>
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</tbody>
</table>

* Average length of indentation in mm

$^\#$ Vickers hardness number assuming an effective load of 37.5 grams
<table>
<thead>
<tr>
<th>Amount of Addition (at.%)</th>
<th>Annealed Condition d*</th>
<th>VHN#</th>
<th>Worked Condition d*</th>
<th>VHN#</th>
<th>Recrystallized Condition d*</th>
<th>VHN#</th>
<th>Recrystallization Temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
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<td>0.1181</td>
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</table>

* Average length of indentation in mm

# Vickers hardness number assuming an effective load of 37.5 grams
### TABLE 13

**Effect of Cold Work on Hardness of Bismuth-Series**

<table>
<thead>
<tr>
<th>Amount of Cold Work(%)</th>
<th>0</th>
<th>0.025</th>
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<th>0.075</th>
<th>0.1</th>
<th>1.0</th>
<th>5.0</th>
<th>10.0</th>
<th>18.0</th>
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</thead>
<tbody>
<tr>
<td>0</td>
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<td>4.05</td>
<td>3.96</td>
<td>4.05</td>
<td>4.15</td>
<td>3.96</td>
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<td>5.05</td>
<td>5.36</td>
<td>5.46</td>
<td>6.75</td>
<td>7.58</td>
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</tr>
<tr>
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<td>-</td>
<td>-</td>
<td>5.38</td>
<td>5.33</td>
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**Hardness after Recrystallization**

| 3.97 | 4.07 | 5.10 | 4.47 | 5.11 | 5.29 | 5.36 | 7.50 | 7.92 | 45 |

- 45 -
### TABLE 3.1

Effect of Cold Work on Hardness of Maximum Solid Solubility Series

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Hardness after Recrystallization:
- 3.97
- 8.13
- 7.92
- 8.81
- 10.17
- 5.36
Fig 3  Hardness of Pure Lead After Cold Work

- - after 3 min
- - after 30 min

Increase in hardness (%)

Amount of cold work (%)
Fig. 4. The Recrystallized Grain Size of the Pb - 0.025% Tl Alloy after 30 Minutes at 20 °C

Mag. . . . 13.3 X
Etchant. : Acetic Acid and Hydrogen Peroxide
Fig. 5 The Recrystallized Grain Size of the Pb - 0.05% Tl Alloy after 30 Minutes at 20 °C

Mag. ... 13.3 X
Etchant: Acetic Acid and Hydrogen Peroxide
Fig. 6 The Recrystallized Grain Size of the Pb - 0.075% Tl Alloy after 30 Minutes at 20°C

Mag. . . . 13.3 X
Etchant: Acetic Acid and Hydrogen Peroxide
Fig. 7  The Recrystallized Grain Size of the Pb - 0.1% Tl Alloy after 30 Minutes at 20°C

Mag. . . . 13.3 X
Etchant. . Acetic Acid and Hydrogen Peroxide
Fig. 8 The Recrystallized Grain Size of the Pb - 1.0% Tl Alloy after 30 Minutes at 90 C

Mag. . . : 13.3 X
Etchant: : Acetic Acid and Hydrogen Peroxide
Fig. 9 The Recrystallized Grain Size of the Pb - 5% Tl Alloy after 30 Minutes at 100 C

Mag.: 13.3 X
Etchant: Acetic Acid and Hydrogen Peroxide
Fig. 10  The Recrystallized Grain Size of the Pb - 10% Tl Alloy after 30 Minutes at 100 C

Mag. . . . 13.3 X
Etchant. . Acetic Acid and Hydrogen Peroxide
Fig. 11  The Recrystallized Grain Size of the Pb - 20% Tl Alloy after 30 Minutes at 100 C

Mag. . . . 13.3 X
Etchant. . Acetic Acid and Hydrogen Peroxide
Fig 12 Effect of Alloying Addition on Hardness
Fig 13 Effect of Alloying & 2.5% Cold Work on Hardness
Fig 14 Effect of Alloying Addition on Recrystallization Temperature

Alloy addition (at. %)

Recrystallization temp. (°C)
Fig. 15 Hardness of Bi-alloys vs. Cold Work
Fig 16  Hardness vs. Cold Work of Max.  
Solid Solubility Limit Series  
- 60 -
DISCUSSION

On cold working the pure lead, it is noticeable that about half of the total hardness increase obtained was achieved with the first 0.5 per cent reduction. The highest percentage increase in hardness was only 40.7 per cent with 6.5 per cent reduction. This small percentage increase in hardness on working is probably due to the high purity of the lead and the relative high deformation temperature (room temperature corresponds to about 0.5 of the absolute melting point of lead). The effect of alloying additions is considered under a series of specific headings.

1) The effect of alloying additions on the recrystallization temperature and hardness

Though many other chemical and physical properties of the solvent and solute atoms affect the solid solubility, the most important factor determining the solid solubility is the difference in size of solvent and solute atoms. Thus the solid solubility varies inversely as the difference. Ludwick found that the unit strengthening resulting from additions of solid-solution-forming elements in lead varied inversely as the solid solubility in lead (i.e., in proportion to the disturbance produced). The same effect was observed here (Fig. 12). However, the percentage increase obtainable in hardness was low on the alloys with the elements of smaller solid solubility (i.e., tellurium), while a larger increase was observed on
the alloys with the elements of larger solid solubility (i.e., bismuth). So, the percentage increases in hardness on a specific alloy was related to the solid solubility of the alloying element.

As expected, the hardness increase levelled off as saturation was reached on the tellurium-series (Fig. 12). From this, it appears that the solid solubility limits were not exceeded in antimony, tin, bismuth and thallium and especially that the maximum amounts added in tin and thallium were well below their solid solubility limits.

The plot of recrystallization temperature against additions (Fig. 14) shows that the curves tend to be S-shaped. For the thallium, bismuth, tin, and antimony series, it is additions in the range of 0.1 to 1.0 per cent that have by far the biggest effect on recrystallization temperature. Hardness measurements of the grain interiors show that it is only above the 1.0 addition level that the grains begin to harden. Thus, when the grains begin to harden, the rate of increase in recrystallization temperature falls sharply.

Since solute atoms segregate preferentially to grain boundaries, where they can be more easily accommodated in the relatively open structure found there, an explanation of the experimental curves follows. The first impurities go to the grain boundaries, but while they are present in
small quantities (less than 0.1 total percentage here for thallium, bismuth, tin and antimony) they do not pin down the boundary. With increasing amount of additions (from 0.1 to 1.0 per cent) a much larger proportion of the boundary is affected by impurity atoms and its movement becomes progressively more difficult. A restriction in grain boundary movement leads to an increase in recrystallization temperature for a given recrystallization time. With still larger amount of additions (more than 10 per cent), the boundary approaches saturation and impurities enter the grain, harden it, and as the grain boundary impurity content levels off, so the recrystallization temperature increase levels off. Thus, the recrystallization temperature is directly related to the impurity content of the grain boundary.

In the tellurium-series, accommodation is so much more difficult that much more distortion and pinning occurs and smaller amounts are required to produce the same effect. The addition of 0.001 per cent tellurium appears to be equivalent to 0.1 per cent in the other instances. Tellurium has a hundred-fold greater effect which compares well with its solid solubility which is of the order of a hundred times less than the others.

The concentration of impurity atoms at the grain boundaries raises the question as to what proportion of the
atoms are boundary atoms. This can not be answered, for it depends on grain boundary width, shape(on an atomic scale), and grain size, and the two former quantities can not be measured as yet.

The greater distortion produced by tellurium probably results in the atom being accommodated over a much narrower boundary width(maybe only 1 to 2 atoms width compared to the others of say 10 atoms width) and saturation comes much sooner.

2) The effect of additions on the amount of cold work necessary for recrystallization at room temperature

The effect of cold work is to deform the grains. Therefore, with increasing amounts of cold work, the grain imperfections increase, hence also the stored energy.

As it is already an imperfect region, the grain boundary is not much affected by cold work except under conditions favoring grain boundary sliding(high temperatures and low strain rates). From the temperature - recrystallization study(Series B), it appeared that, for up to 0.1 per cent alloying addition, the alloying element was concentrated at the grain boundaries. Under these conditions, with little amount of alloying element in the grains, the amount of work necessary for recrystallization should not change much as grains are little changed. This is verified experimentally with the bismuth-series where up to 0.1 per cent bismuth
has little effect on the amount of cold work required for recrystallization.

With additions of bismuth of between 0.1 and 5 per cent, the amount of cold work necessary for recrystallization increased rapidly (Fig. 17). It is during this stage that the hardness of the grain itself increases sharply. With the growing accumulation of impurities in the grain, the individual grains are becoming progressively more distorted, so the initial energy state of the grain before cold work is increased. Thus, if a specific amount of excess energy from cold work is needed for recrystallization to occur, the amount of cold work necessary for recrystallization will progressively increase. The work on pure lead shows that the first part of the curve has by far the biggest effect, that is, the first imperfections introduced affect the properties most. When the impurity ceases to affect hardness, it does not alter the deformation necessary for recrystallization.

It was noticed that the use of hardness change, as a quantitative rather than qualitative means of following the effect of alloying addition on the amount of cold work for recrystallization, has limitations, mainly because of

(1) The arbitrary nature of the measurement arising from load, indentation, angle of diamond pyramid, etc.

(2) The complex mode of the deformation caused by
the indentations.

(3) The uneven distribution of hardness between different grains depending on their orientation.

For the maximum solid solubility series (Series C Part 2), a general trend was found that a higher amount of work for recrystallization was needed for the alloy with an element of larger solid solubility. A comparison of the results with tellurium (maximum 12.5 per cent) and thallium (maximum 50 per cent) illustrates this. However, the uncertainty of the exact solubility limits prevents a more detailed analysis.

All experimental results indicate that the solid solubility of tin in lead is larger than that of antimony (see Figs. 12 - 14).

3) Grain size after recrystallization

In high alloys, full softening did not occur after recrystallization. This was due to the fine grain size after recrystallization which, in turn, led to harder values. The higher the alloy content, the finer was the grains (see Figs. 4 - 11). This fine grain size probably resulted because of the fixed time (30 minutes) for measurement. Since the rate of grain growth is slow for the high alloys, there might be little chance for a grain to grow after recrystallization. Slowness of grain growth arises from the drag on the grain boundaries of the impurity.
4) Significance of results compared to the recrystallization theories

The theories of recrystallization are very general and have not been placed on a sound quantitative basis. Their point of disagreement is the origin of the small region from which recrystallization proceeds. From the present study two points emerge which if confirmed will help establish a more fundamental model.

(1) Below a minimum amount of alloying, which depends on the solid solubility limit of the metal, additions do not affect the recrystallization temperature. A range then follows where the recrystallization temperature increases sharply with alloy content, but this then levels off when the grain hardness begins to rise.

(2) Until sufficient alloy is added to harden the grain the amount of work necessary for recrystallization is little changed.

This implies that the recrystallization temperature for a given time (conversely, recrystallization time at a given temperature) depends directly on the locking effect of the grain boundary by impurities. If there are insufficient impurities to exert a drag on the boundary, the recrystallization characteristics are unchanged. Once the boundary is saturated with impurities, the drag effect...
becomes constant, as does the recrystallization temperature. The driving force is the excess distortion energy of the grain introduced by cold work, the rate controlling factor is grain boundary movement. If the grain is already distorted by alloy additions, more work is needed.

A grain boundary migrates from a low energy region into higher energy areas thereby causing recrystallization. The low energy block hypothesis with a pre-existing undeformed low energy region thus seems wholly adequate to explain the mechanisms of recrystallization. The presence of jogs along grain boundaries across which compressive stresses are developed during deformation could lead to such a small block as shown by Davies, Greenough, and Wilshire.\(^{(65)}\) In any given alloy, the concentration of impurities at a grain boundary will be a function of the relative grain orientation and of temperature,\(^{(66)}\) thus the combined impurity amounts will not necessarily be constant.
Fig 17 Effect of Alloying on the Amount of Cold Work Necessary for Recrystallization at R.T.
SUGGESTIONS FOR FURTHER WORK

The following experiments can be suggested to obtain a more complete understanding of the characteristics of recrystallization in lead.

1) By measuring directly impurity concentration at the grain boundary in the early stages, by means of an instrument such as a microprobe analyser, the exact effect of alloying additions on hardness and on anchoring of grain boundary, thus on recrystallization behavior, can be examined. The effect of an alloying element on hardness can also be examined by using single crystals (i.e., by comparison with polycrystals, determining the amount of impurity needed to saturate the grain boundary).

2) Since the total grain boundary area is related to the grain size, the effect of alloying additions on hardness and recrystallization behavior can be examined using a wide range of initial grain sizes.

3) A more comprehensive study on recrystallization behavior of lead can be pursued by using a wide range of temperatures (such as the liquid nitrogen temperature), and with a wider range of alloying additions. Possibly all the elements with solid solubility in lead more than 20 parts per million (see Table 2) can be used. However, again the exact solid solubility is known in very few instances.
CONCLUSIONS

1) The recrystallization temperature of a lead alloy is directly related to the maximum solid solubility of the added element.

2) Limits exist both above and below which addition have little effect on recrystallization, because they have little effect on grain boundary movement.

3) The increased amount of cold work necessary for recrystallization at a given temperature after alloying depends solely upon the hardening produced by the alloying.

4) It is unlikely that the recrystallization temperature of lead can be raised much above 150°C (which corresponds to 0.7 of absolute melting point of lead).
REFERENCES

1) Kalisher, R. "Ber. dtscb Chem Ges" 14/2 p. 2747 1881

2) Sachs, G., & Van Horn, K. R. "Practical Metallurgy" Cleveland, U. S. A. 1940

3) Burke, J. E. "The Fundamentals of Recrystallization and Grain Growth in Grain Control in Industrial Metallurgy" Cleveland, U. S. A. No. 1 1948


5) Burke, J. E., & Turnbull, D. "Prog. in Met. Phys." vol. 3 p. 220 1952

6) Beck, P. A. "Metal Interfaces" ASM Seminar Cleveland, U. S. A. p. 208 1952

7) Beck, P. A. Advances in Phys. vol. 3 p. 245 1954


19) Dunn, C. G., & Daniels, F. W. Trans. AIME vol. 191 p. 147 1951
21) McLean, D. "Mechanical Properties of Metals" Wiley See Fig. 8.14 p. 282 1962
23) Petersen, C. Metalfforschung vol. 2 p. 289 1947
27) Cottrell, A. H. Prog. in Metal Phys. vol. 4 p. 205 1953
33) Stanley, J. K., & Mehl, R. F. Trans. AIME vol. 150 p. 260 1942

- 73 -


36) Lücke, K., & Detert, K. Acta. Met. vol. 5 p. 628 1957


39) Smith, C. S. "Metal Interfaces" ASM Seminar Cleveland, U. S. A. p. 65 1952


42) Burke, J. E., & Shiau, Y. G. Trans. AIME vol. 175 p. 141 1948


46) Singleton, W., & Jones, B. J. Inst. of Met. vol. 51 p. 71 1933


48) Beck, P. A. Trans. AIME vol. 137 p. 222 1940


- 74 -
50) Loofs - Rassow, E. Metallwirtschaft vol. 10 p. 61 1931

51) Butler, J. M. J. Inst. of Met. vol. 86 p. 155 1957 - 58

52) Hirst, H. J. Inst. of Met. vol. 66 p. 39 1940


56) Smart, J. S., & Smith, A. A. Trans. AIME vol. 147 p. 48 1942

57) Smart, J. S., & Smith, A. A. Trans. AIME vol. 156 p. 144 1946


60) Werner, H. W., & Worner H. K. J. Inst. of Met. vol. 66 p. 45 1940

61) Gifkins, R. C. Metallurgia p. 209 April, 1961

62) Bol'shanina, M. A., & Elsukova, T. F. Zavodsk Lab vol. 30(3) p. 315 1964


64) Ludwick, F. Zeitschrift für anorganische und allgemeine chemie vol. 94 p. 161 1916

65) Davies, P. W., Greenough, A. P., & Wilshire, B. Phil. Mag. vol. 6 p. 795 1961


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GLOSSARY

The following is a brief explanation of technical terms as used in this thesis.

Annealing:
A heat treatment process to obtain a fully softened recrystallized metal.

Burgers vector:
The slip vector distinguishing a sheared region from the rest of a crystal. This is a characteristic property of a dislocation.

Cold work:
The plastic deformation of a metal or an alloy below the recrystallization temperature.

Dislocation:
A line defect in a crystalline material, the movement of which leads to plastic deformation.

Polygonization:
A recovery process occurring in crystals that have been plasticly deformed. This involves the rearrangement of dislocations into low-angle boundaries, thus lowering the strain energy.

Slip line:
The surface trace of displaced lattice rows after plastic deformation.

Stacking fault:
A ribbon of hexagonal close packed structure in a face centered cubic crystal (or vice versa).

Twining:
A mechanism whereby two crystal lattices are related to each other in orientation as mirror images.

Vacancy:
A point defect(hole) in a crystalline material where an atom should be.