ORDERING IN β COPPER-TIN ALLOYS

A

Thesis

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- by -

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The isothermal decomposition products of hot worked $\beta$ and $\gamma$ copper tin alloys have been studied after varying times at different annealing temperatures. Electrical resistivity temperature curves have been measured on heating the hot worked alloy through the $\beta$ and $\gamma$ regions, as has the effect of annealing in these regions on the as quenched electrical resistivity. The crystal structures of the phases observed have been examined at temperature, briefly, and on quenching to room temperature.

The effect of small additions of nickel on the $\beta$ and $\gamma$ phase has been examined using identical techniques to those applied to the binary alloys.

It has been shown that the decomposition products of the 26 and 27 tin alloys depend, after hot working, on the annealing time at temperature and that the change in decomposition products can be correlated with the $\beta$ to $\gamma$ transformation and ordering of the $\beta$ phase. Changes observed in the electrical resistivity of the $\beta$ and $\gamma$ phases can be correlated with the effects observed during isothermal transformation but the resistivity of the phases retained by quenching is difficult to interpret due to the complicating factors of martensite formation and possibly vacancy retention.

The structure of the $\beta$ phase retained by quenching has been
shown to have an ordered body centred cubic structure associated with varying amounts of martensite.

The addition of nickel results in the formation of a two phase \((\rho + \gamma)\) region not observed in the binary alloys, but otherwise similar effects are found.

A modified binary copper tin has been suggested in the light of the results obtained.
Grateful thanks are due to Mr. L. W. Derry, Dr. A. F. Kiedowsnik, Mr. J. F. Towner and other friends and colleagues at Battersea College of Technology for encouragement and advice; to Dr. W. Eliaš for assistance in translating many foreign articles and for use of the vacuum quenching apparatus; to Dr. Robbins and Dr. Pyrthofürh of the Tin Research Association for the preparation and analyses of the alloys; to Professor F. C. Thompson for helpful suggestions; and to the Department of Scientific and Industrial Research for financial assistance.
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INTRODUCTION

The copper tin system has been the subject of numerous investigations during the past century. Despite these, the relationship existing between the $\beta$ and $\gamma$ phases of this system is still not completely understood. During more recent years it has been suggested that $\gamma$ is an ordered form of $\beta$. It was the primary object of this research to investigate the $\beta$/$\gamma$ reaction, to confirm or reject the possibility of ordering and to establish the relationships between this reaction and other associated reactions.

The $\beta$ phase is an electron compound, stable under equilibrium only at high temperatures and based on the 312 electron to atom ratio with a body centred cubic crystal structure.

The $\gamma$ phase, which according to the current phase diagram forms from the $\beta$ phase by a eutectoid reaction, is also a high temperature phase existing at higher tin contents than the $\beta$ phase. Until recently, it has also been reported to have a body centred cubic crystal structure.

Between the $\beta$ and $\gamma$ phase fields in the current phase diagram there is a narrow two phase ($\beta + \gamma$) field but the experimental evidence for this region is very limited. For instance, in a review of the literature Raynor \(^1\) stated that "the location of the ($\beta + \gamma$) field is not exactly established experimentally but cannot differ greatly from that shown in the figure" (reproduced as Fig.1.1).

Following the literature search, (which is reviewed in Chapter I) it was thought advisable as a preliminary to attempt to define the
(β + γ) phase region. Alloys were therefore quenched from temperatures in and around the (β + γ) field (Fig. 1.1.) polished and etched in alcoholic ferric chloride and examined microscopically. In all cases only a single phase alloy was found, although sub-boundaries were observed occasionally. Other etchants were tried, notably:

- 1% aqueous chromic acid
- Phosphoric acid - sulphuric acid mixtures
- Nitric acid in methyl alcohol
- Ammonia

A solution of 45% phosphoric acid, 15% sulphuric acid, 7.5% saturated aqueous chromic acid in water, 32.5% water.

These solutions were selected either because it had been stated that they etched or polished similar materials or because they selectively attacked either copper or tin. They were all tried with and without an e.m.f. but, whenever etching occurred, only a single phase structure was observed.

As the β and γ phases appeared identical and a microscopic two phase (β + γ) field could not be found, it was considered that if there were a difference between β and γ it should become evident by an examination of their mode and kinetics of decomposition.

A study was therefore started on the decomposition products of the β and γ phases and, because ordering was suspected X-ray diffraction and electrical resistivity were used as ancillary techniques.

A literature search on the effect of ternary additions indicated that certain minor ternary additions do result in a microscopic two phase
(\(\rho + \gamma\)) field and the research was extended to study the effect of small nickel additions on the above properties.

In accordance with the development of this investigation, the description and interpretation of the research is reported in the sequence of previous work, design and development of apparatus, the results obtained, a discussion of the effects observed and the conclusions.
**FIG. 1.1. - THE COPPER TIN PHASE DIAGRAM**

Tin atomic per cent

**Point** A B C D E F G H I J K L

°C 798 798 798 755 755 755 586 586 586 520 520 520

Wt.% Sn 13.5 22.0 25.5 25.9 27.0 30.6 15.8 27.0 25.4 15.8 27.0 32.4

At.% Sn 7.7 13.1 15.5 15.8 16.5 19.1 9.1 14.9 15.4 9.1 16.5 20.4

Point M M' N N

°C 350 200 350 350

Wt.% Sn 11.0 1.2 32.5 37.8

At.% Sn 6.2 0.7 20.5 24.6
CHAPTER I

A LITERATURE REVIEW

SECTION 1. The constitution of the copper tin system.

The currently accepted equilibrium diagram, compiled by Raynor is reproduced as Fig. 1.1. The β phase is shown on this diagram as a narrow range of composition occurring under equilibrium only at high temperatures. The diagram shows that the β may be formed on solidification either directly from the melt or by the peritectic reaction $\alpha + L \rightarrow \beta$ and further that β may decompose by another peritectic reaction $\alpha + L \rightarrow \gamma$. In the solid state β decomposes to mixtures of $\alpha + \gamma$ by precipitating the primary phase $\alpha$ or $\gamma$ according to composition and then finally by a eutectoid reaction $\beta \rightarrow \alpha + \gamma$ at 586°C. There is considerable doubt about the validity of this eutectoid reaction; therefore during this research, it will be called the '586°C. arrest'. The results which led to this phase diagram have been reviewed and a summary is given emphasising the more important points. To do this it is convenient to divide the subject matter into three parts, namely:

A. Evidence for a reaction at 586°C. in alloys containing from 16-25% Tin.

B. Evidence for the ($\beta + \gamma$) field.

C. Evidence for the peritectic reaction $\beta + \text{Liq.} \rightarrow \gamma$
A. Experimental evidence for a reaction at 586°C in alloys containing from 16-25% tin.

i. By Thermal Analysis

Several workers 2,3,4,5,6, have performed thermal analysis experiments on alloys of this composition and without exception have observed an evolution of heat at approximately 586°C on both heating and cooling curves; although some 4 stated that a high temperature anneal at 700°C - 750°C was necessary, otherwise the effect was very faint. Figure 1.2. shows a typical arrest for a 23% alloy - the second smaller arrest at a higher temperature corresponds to the evolution of α due to the change in solid solubility on cooling. The size of the heat evolution at 586°C increased with increasing tin content to a maximum at approximately 25% tin and then decreased very rapidly to zero as the tin content was further increased. This is consistent with increasing amounts of α being precipitated during the reaction as the tin content increases and indicates that the specific heat of the β to γ change is very small.

ii. By Electrical Resistant measurements

Electrical resistance temperature curves 5,6,7, obtained for these alloys indicate a change in the temperature coefficient of resistivity at approximately 586°C, as indicated in Fig. 1.2. The maximum effect again occurred in alloys of about 25% tin while it
The following figure illustrates some effects observed in copper tin alloys by past workers.

**Fig. 1.2.** A schematic diagram showing some effects observed in copper tin alloys by past workers.
was not generally detected in alloys of higher tin content.

iii. By Metallographic Examination

Microscopic examination by, has shown that during this reaction at 586°C, only is precipitated from the \( \beta \). It takes the form of colonies and may be associated with a sub-graining of the \( \beta \). No other phase has been observed.

E. Experimental evidence for the \( (\beta + \gamma) \) field.

i. By Thermal Analysis

Many workers, 10, 8, 4, 11, carrying out thermal analysis work in this region have been unable to find any evidence for the \( (\beta + \gamma) \) field, only Namasumi and Odamura by using very careful differential thermal analysis, were able to find any indication of a change. Their curves which give fairly consistent results and show only one arrest, are reproduced in Fig. 1.4. and the temperature of the arrest on Fig. 1.3.

ii. By Electrical Resistance measurements.

The results of electrical resistance temperature measurements in this region are very confused and may best be summed up by reference to Fig. 1.3, which contains the results obtained by all the workers. The temperatures plotted were obtained from slight slope changes in resistance temperature curves (ref. Fig. 1.2.) Closer examination shows that two groups of workers 6,13, were
FIG. 1.3. EXPERIMENTAL EVIDENCE FOR THE $\beta + \gamma'$ FIELD

Thermal arrests

- Hamasumi and Odamura\textsuperscript{12}

Electrical Resistance Changes

- Hamasumi and Nishigori\textsuperscript{11}
- Vero\textsuperscript{8}
- Isihara\textsuperscript{7}
- Matsuda\textsuperscript{14}
- Imai and Obinata\textsuperscript{6}
- Hosoi\textsuperscript{13}

Arrows indicate rising or falling temperature respectively.
unable to find any change while an investigation into the techniques of the others reveals several anomalies. The analysis of an alloy used by Yero revealed a composition gradient of 26.4% to 27.1% tin from one end to the other. He used long (about 12 cm) as cast and annealed specimens, as did all the others.

Kanasumi and Hishigori in 1931 found a change in the field as shown, which they interpreted as a "superstructure change" and put the field in the region shown dotted (Fig. 1.3) as a result of metallography and thermal analysis. However, on summing up his researches in 1937 Hamasumi as a result of the differential thermal analysis mentioned above, ignored these results and redrew the field in the conventional position.

Isihara also placed the field in the general region shown dotted, as the result of resistance temperature curves. He interpreted the 506°C arrest as a change in the phase because he alone found a small change in the resistance curves in the region. Matsuda however, showed that this change was due to the silver contact wires used by Isihara and was not reproducible with iron, copper or platinum contact wires.
25% Sn
260°C Sn
600°C to 577°C
100°C lower peak
after cooling 2-27/10°
550°C 
200°C peak
after cooling 2-81/10°
541°C
600°C peak
after cooling 2-571°
895°C
100°C lower peak
after cooling 2-37/10°
639°C

27% Sn
28% Sn
600°C lower peak
after cooling 4-45/10°
696°C
620°C peak
after cooling 4-57/10°
696°C
640°C peak
after cooling 4-17/10°
720°C
100°C lower peak
after cooling 2-25°
733°C
120°C lower peak
after cooling 11-27/10°
733°C

Fig. 1 Effect of Quenching on the Electrical Resistance of β Tin Bronze

Differential Thermal Analysis Curves Obtained by Hanasaki & Odamura

Electrical Resistivity Temperature Curves Obtained by Hosoi
Kosoi was the only worker to carry out his resistance measurements on quenched specimens and his results are plotted in Fig. 1.5. The deflection in alloy 4 (25.1% Sn) is included in Fig. 1.3, although it appears doubtful from the microstructures described by Kosoi, if full retention of the high temperature structure was obtained.

iii. By Metallographic Examination

Some workers have based the positioning of the \((\beta + \gamma)\) field on the evidence of quenched microstructures. Alloys rapidly quenched from the \((\beta + \gamma)\) field (Fig. 1.1) have been shown to be microscopically single phase at least with the etches used. However, the critical cooling velocity for retaining \(\beta\) or \(\gamma\) is high and increases rapidly with increasing tin content, the photomicrographs published, purported to be \((\beta + \gamma)\), invariably contain complex dark etching mixtures but never a simple two phase alloy. It appears therefore, that these structures have resulted from slack quenching.

The appearance of an acicular martensitic phase in quenched alloys of less than 24.3% tin (Sutectoid composition Fig. 1.1) and a retained \(\beta\) or \(\gamma\) structure in alloys with greater than 24.3% tin, has been used by some to indicate
the \( \beta - \gamma \) change. Kurdjumov\textsuperscript{17} has determined the martensite start temperatures (\( K_s \)) for these alloys using X-ray techniques and found that the \( K_s \) decreases very rapidly with increasing tin content so that alloys with less tin than 24.8\% have an \( K_s \) above room temperature while those with more tin have an \( K_s \) below room temperature. The observation of a martensite by metallography has also been shown to depend on the etchant used\textsuperscript{11}.

iv. \textbf{By X-ray Examination}

For many years, despite speculation of a superlattice, the crystal structures of both \( \beta \) and \( \gamma \) as revealed by X-rays were determined as simple body centred cubic. The lattice parameters obtained by all previous workers are plotted in Fig 1.6, the higher values, over \( 3 \, \text{\AA} \), are applicable to measurements at temperature while the remaining values apply to quenched specimens. In the high temperature results there is marked disagreement between the results of Isawa\textsuperscript{18} and those of other workers. His results taken at the lowest temperature used, give lattice parameters approximately 0.03 \( \text{\AA} \) larger than the remainder. It is difficult to account for this discrepancy, which is far larger than the difference between \( \text{\AA} \) units and Angstroms, other than by assuming an error in constant. The quenched lattice parameters obtained
Fig. 1.6. The variation of the lattice parameter of the β phase with composition.
in the same research are also higher. Isawa did however obtain extra lines in his high temperature photographs but was unable to interpret them.

Recently the crystal structure of the Y phase has been reported as ordered body centred cubic by Hendus and Knodler \(19\), who stated that the order is based on the stoichiometric composition \(\text{Cu}_2\text{Sn}\) at 25 atomic per cent tin (38 weight per cent tin) which is at the composition of the \(\varepsilon\) phase. This order, which is of the \(\text{DO}_3\) type analogous to \(\text{Fe}_3\text{Al}\), extends on the low tin side as far as 15 atomic per cent tin (25 weight per cent tin) at 700°C. The lattice parameter composition curve is shown dotted in Fig. 1.6 with a slight curve as suggested by Hendus and Knodler although they only reported the two extreme values. The ordered cell which is face centred cubic with twice the lattice parameter of the disordered cell, is shown in Fig. 1.7.

The crystal structure of the martensite phases formed on quenching \(\beta\) and \(\gamma\) also depend upon composition \(17\). Below 24.75 tin the martensite has a hexagonal type lattice whose crystal structure is not fully determined, while above 25.35 tin the structure is orthorhombic and between the two compositions there is a mixture of the two structures. The structures are analogous to similar martensites formed on quenching the \(\beta\) phase in copper aluminium alloys.
F.C.C. Superlattice cell

Disordered B.C.C.

Ordered Unit Cell Cu$_3$Sn

Fig. 1.7.
C. Experimental Evidence for the peritectic reaction $\beta + \gamma' \rightarrow \gamma$

i. By thermal analysis.

Thermal analysis $4, 8, 10$ of alloys containing from 25 to 30% tin has consistently indicated an arrest during solidification at approximately 755°C. This arrest has invariably been interpreted as a peritectic reaction. Verčy $5$ suggested that there were two arrests and therefore two peritectic reactions and as a result included both two phase regions as indicated on Fig. 1.3. That is, a conventional $(\beta + \gamma)$ field and another $(\gamma + \alpha)$ region shown dotted but this has been disproved (see below).

ii. By Electrical Resistance measurements

The only other reported work on the reaction was by Namasymi and Takamoto $20$ and they performed electrical resistance - temperature curves in this region largely to check the work of Verčy. Their results are shown in Fig. 1.8 and indicate that there is only one reaction at least as observed by resistance measurements. They also interpreted these results as a peritectic reaction.
FIG. 1.8. ELECTRICAL RESISTANCE TEMPERATURE CURVES OBTAINED BY HAMASUMI AND TAKAMOTO DURING MELTING AND SOLIDIFICATION AND THE DERIVED PHASE DIAGRAM.
The modes of decomposition of the $\beta$ and $\gamma$ phases.

In view of the difficulty of distinguishing between the $\beta$ and $\gamma$ phases, it was considered that some indication of the differences between them might be obtained by examination of their decomposition products. The literature search was therefore extended to cover this aspect and work in this field was found to be of two types:

A. Isothermal decomposition of the $\beta$ or $\gamma$ phases.

B. The Tempering of quenched $\beta$ or $\gamma$.

A. Isothermal decomposition of the $\beta$ or $\gamma$ phases.

Three workers 9, 21, 22, have used this method to study the decomposition of $\beta$ and $\gamma$ bronzes but none of them have investigated the effect of varying the annealing temperature. Nagasaki 22 and Hosoi 21 reported their work in Japanese language journals, but neither made any reference in the synopsis to the solution temperature.

Nagasaki 22 examined alloys containing 22, 23, 25, 26 and 28% Sn and obtained the S curves which are reproduced in Fig. 1.9.

He concluded that the transformations in the hypoeutectoid alloys were upper bainitic above 350°C, and lower bainitic below 350°C, while the hypereutectoid alloys were pearlitic with proeutectoid occurring at temperatures a little below the eutectoid temperature.

He also stated that transformation in the latter alloys was very rapid and this made examination difficult. A martensitic structure
FIG. 1.9. THE ISOTHERMAL TRANSFORMATION CURVES OBTAINED BY NAGASAKI 22

FIG. 1.10. THE ISOTHERMAL TRANSFORMATION CURVES OBTAINED BY HOSOI 21
occurred in the 22 and 23.5\% tin alloys at 150° and 100°C, respectively and during immersion in liquid oxygen in the 25 and 26\% tin alloys. He explained his results on the basis of a metastable diagram.

Hosoi\(^2\) obtained 'S' curves on alloys of 25.08, 26.38 and 27.31 tin (Fig.1.10) and considered them analogous to Nagasaki's curves. He also examined these alloys by hardness and electrical resistance measurements. Hardness measurements were taken at room temperature on alloys isothermally treated at various temperatures for increasing times. At and above the 'nose' temperature the curves showed a single hardening peak while at 'sub-nose' temperatures two stage hardening was observed (Fig.1.11.). The resistance measurements consisted of tempering curves performed on alloys isothermally treated at several temperatures for various times Fig.1.12. The curves indicate that if the alloy is treated so as not to transform, e.g. 10 seconds 400°C, there is a large decrease in resistance at 350°C on tempering, but if the alloy is transformed the decrease is either absent or made much smaller.

Hidcownik\(^9\) isothermally transformed a 25\% tin alloy after annealing for 15 minutes at 700°C. Largely to correlate the results with those obtained by continuous cooling the same alloy. The 'S' curve he obtained is shown in Fig.1.14. and is similar in form to those of Nagasaki and Hosoi, although it does introduce
FIG. 1.11. HARDNESS CHANGES DURING ISOTHERMAL TRANSFORMATION OF A 27.31% TIN ALLOY
HOSOI 21.

Fig. 1.13. T.T.T. diagram obtained for a 24.2% tin bronze by Miodownik.*
the additional factor of sub-boundary formation during transformation. He did however, briefly examine the effect of varying the quenching temperature on some end quenched alloys and reported that the structures were unchanged but that the maximum hardness of the product increased with increasing annealing temperature at intermediate cooling rates. He attributed this qualitatively to the normal effect of varying the heat treatment temperature.

II. The Tempering of \( \beta \) or \( \gamma \) obtained by quenching.

This method has been used by several workers \( 6,18,22,23,24,25 \) to study the decomposition of the quenched martensitic, retained \( \beta \) and \( \gamma \) structures but again no attention has been paid to the effect of quenching temperature.

There is general agreement on the variation of the properties of hardness, resistance and specific heat with temperature and composition as exemplified in Fig.1.14 but the interpretation of these changes is not well defined. Isowa has suggested a decomposition sequence \( \beta \rightarrow \beta^* \rightarrow \alpha + \delta \) while Imai and Ohinata\( ^{6} \) have suggested a two stage process \( \beta \rightarrow \beta^* \rightarrow \beta^{**} \rightarrow \alpha + \delta \) corresponding to the two small peaks in the specific heat curve. X-ray work by Kosoi\( ^{25} \) identified \( \beta^* \) at 250ºC. as \( (\beta + \alpha) \) or \( (\beta + \delta) \) according to whether the alloy was hypo or hyper eutectoid but he could not identify \( \beta^{**} \) which was different to \( \beta^* , \beta , \alpha + \delta \) and had the lowest specific resistance.
FIG. 1.14. THE VARIATION OF ELECTRICAL RESISTIVITY, SPECIFIC HEAT, HARDNESS AND STRUCTURE WITH COMPOSITION AND TEMPERATURE ON TEMPERING QUENCHED β BRONZES.
It is worth noting that none of these workers have considered the \((\alpha + \gamma)\) eutectoid in the interpretation of their results. Prior to the work of Owen and Iball\(^{23}\) in 1935, the \(\gamma\) phase was thought stable down to room temperature. Owen and Williams\(^{29}\) later showed that annealing powdered samples with between 17.5 and 36% tin, transformed them completely to after five to seven days at 300°C. However, Wong and Hansen\(^{30}\) showed that annealing an \((\alpha + \gamma)\) structure in block form for sixty three days at 300°C produced only about 5% decomposition of the \(\gamma\) phase.
SECTION III. The effect of ternary additions on the Copper Tin phase diagram.

As the result of a literature search, it was found that the effect of several ternary additions on the copper tin diagram has been studied and these will now be briefly reviewed in relation to their effect on the $\beta$ and $\gamma$ phase fields of the binary alloy and their decomposition products.

i. Aluminium

The copper corner of the copper tin aluminium diagram has been studied extensively by Leach. He found that above 650°C, the $\beta$ phases of the copper tin and copper aluminium systems form a continuous solid solution. With less than 2% aluminium he was unable to distinguish between $\beta$ and $\gamma$ although he tried several different etching solutions, and quenching temperatures between 572°C and 672°C. With greater than 2% aluminium he was only able to differentiate $\beta$ and $\gamma$ by the decomposition products on quenching; $\beta$ forming a martensitic structure and $\gamma$ a eutectoid decomposition product.

ii. Antimony

On adding antimony to the copper tin alloys the $\beta$ phase gradually decreases in stability becoming non-existent very near to the binary copper antimony diagram while the $\gamma$ phase forms a continuous solid solution with the $\beta$ Cu$_3$Sb phase field. This has a D-O$_3$ superlattice structure analogous to the structure
suggested by Hendus and Knodler\textsuperscript{19} for \( \gamma \) copper tin alloys.

iii. Beryllium

The effect of \( 1\% \) beryllium is to raise the decomposition temperature of the \( \beta \) phase from 586\(^\circ\)C to 650\(^\circ\)C according to Rowland and Upthegrove\textsuperscript{34} but as alloys of high beryllium content were not examined, the further effects are unknown. A microstructure of \( (\beta + \gamma) \) is presented which indicates that a two-phase region exists in these alloys.

Decomposition of \( \gamma \) results in the formation of an additional phase \( \Theta \) which is said to be micrographically similar to the \( \Theta \) phase formed in copper tin nickel alloys.

iv. Manganese

The addition of manganese results in considerably increased stability of the \( \beta \) phase. Ordering occurs widely around the composition \( \text{Cu}_2 \text{SnMn} \) and a ferromagnetic Heusler type alloy results\textsuperscript{35}. No work appears to have been done on the \( (\beta + \gamma) \) region and the relationship between the \( \gamma \) region and the ordered \( \text{Cu}_2 \text{SnMn} \) region is unknown.

Decomposition of the \( \beta \) phase results in the formation of \( \gamma \) prime\textsuperscript{\( h \)}, which was called \( \Theta \) by Funk and Rowland\textsuperscript{43} (compare \( \text{CuSnNi} \)). This phase was metallographically similar to \( \gamma \) but had a hexagonal crystal structure.
v. Nickel

The addition of nickel increases the decomposition temperature of the β phase markedly, so that in alloys with greater than 5% nickel it is not observed. Alloys containing 2% nickel quenched from the (β + γ) region have been shown to be two phase. Miodownik, using an end quench technique, studied the decomposition of an alloy containing 1.5% nickel which at soaking temperature consisted of (β + γ) and found that the products were very similar.

Thermodynamic data indicates that the binary compound Ni₃Sn₂ is the most stable in this system and, according to Veselka, merges across the diagram with the γ phase of the copper tin system. However, there is some disagreement over this because Nash and Upthegrove state that γ decomposes to Θ (ref. Cu Sn₂) at low tin concentrations. Raynor has suggested that Θ is Ni₃Sn₂ by phase boundary analysis of Nash and Upthegrove's work. Nash and Upthegrove also suggest a modification in the structure of the θ phase as a result of adding nickel. They examined the alloys under polarised light and concluded that θ (Cu Sn Ni) was anisotropic and therefore probably a tetragonal or hexagonal form of θ.

vi. Phosphorus

Phosphorus has no effect on the β or γ phases. It introduces the compound Cu₃P into the microstructure as the
ternary 'eutectic'.

vii. Silver

As silver and copper have unfavourable size factors there is only a limited solubility for silver in all copper tin alloys and this has little effect on the $\beta$ and $\gamma$ phases.

viii. Zinc

In the copper tin zinc phase diagram, the $\beta$ phases of the binary alloys form a continuous series of solid solutions as do $\delta$ (Cu Sn) and $\gamma$ (Cu Zn) phases. The transformation at 506°C in the copper tin diagram has been shown to be continuous with the $\beta\rightarrow\beta'$ ordering of the copper zinc system.
The salient points arising out of the literature survey are:

1. There is a horizontal thermal arrest occurring in alloys containing from 16% to 25% tin.
2. There is no conclusive evidence for a $(\beta + \gamma)$ two phase field or any phase change in this region of the binary alloys. High temperature resistivity measurements have proven very inconsistent while low temperature work, although more hopeful, is difficult because of the rapid decomposition of these alloys.
3. There is an arrest at approximately 755°C corresponding to a peritectic reaction but there is little proof of this interpretation.
4. In general, ternary additions which form a disordered B.C.C. structure with copper make a continuous solid solution with the $\beta$ phase while those which form an ordered B.C.C. structure with copper, make a continuous solid solution with the $\gamma$ phase.
5. The addition of small amounts of some ternary elements results in a microscopic two phase field close to the region suggested for the binary $(\beta + \gamma)$ field.

In addition to this, all workers seem to have been plagued with inherent difficulties associated with the very high decomposition rate of the $\beta$ and $\gamma$ phases and the extreme brittleness of the decomposition products of $\beta$ and $\gamma$ and of $\gamma$ itself above 27% tin. This has resulted in workers using cast specimens which, although well annealed, have almost certainly been segregated to
a varying degree.

With this in mind it was decided to attempt a re-investigation of this part of the system using the following experimental procedures:

1. An isothermal study of the decomposition behaviour of $\beta$ and $\gamma$ by soaking at temperatures in the $\beta$, $(\beta + \gamma)$, and $\gamma$ fields, Fig. 1.1, and studying the nature and rates of formation of the $(\alpha + \delta)$ product.

2. A study of electrical resistivity measurements at high and low temperatures.

3. A study of the crystal structure of quenched alloys.

In all this work, alloys containing a small percentage of nickel to introduce a duplex $(\beta + \gamma)$ field, would be used, as well as the simple binary alloys.
CHAPTER II
THE EXPERIMENTAL TECHNIQUES

SECTION 1 The preparation of alloys.

The melting and analysis of the alloys (Table 2.1.) was very kindly performed by Dr. Pyrtherch of the Tin Research Association. Nominal compositions were chosen by reference to the phase diagram to include all possible relevant structures. Nickel alloys were made at a later stage by taking the most useful binary alloy compositions, keeping the tin content constant and adding 1 and 2 atomic per cent nickel in place of copper.

Melts of approximately 500 gm. were prepared, either under vacuum, or in a high frequency furnace as indicated below, annealed for 4 - 6 hours and then hot rolled in the β region to bars between 1/10" and 1/16" thick, so that every alloy had greater than 90% total reduction. In view of the comparatively narrow temperature range of the β phase and the size of the bars, this process required considerable care and technical skill; even so, alloys with greater than 27% tin were broken and severely cracked down the edges.

The as received alloys were heated at 600°C. for half an hour, furnace cooled, polished along their whole length, etched and examined under the microscope for changes in composition. This method is in fact more accurate than might be imagined because quite
<table>
<thead>
<tr>
<th>Tin</th>
<th>Nickel</th>
<th>Tin</th>
<th>Nickel</th>
</tr>
</thead>
<tbody>
<tr>
<td>23</td>
<td>-</td>
<td>22.9</td>
<td>-</td>
</tr>
<tr>
<td>25*</td>
<td>-</td>
<td>24.7</td>
<td>-</td>
</tr>
<tr>
<td>26</td>
<td>-</td>
<td>25.8</td>
<td>-</td>
</tr>
<tr>
<td>27*</td>
<td>-</td>
<td>26.8</td>
<td>-</td>
</tr>
<tr>
<td>28</td>
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<td>-</td>
</tr>
<tr>
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<td>24.3</td>
<td>0.8</td>
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</tr>
<tr>
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<td>23.0</td>
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</tr>
<tr>
<td>27</td>
<td>1.6</td>
<td>27.3</td>
<td>1.7</td>
</tr>
</tbody>
</table>

Table 2.1. Alloys used during this investigation

All alloys except those indicated * were vacuum melted.
small changes in composition result in a change from primary \( \alpha \) to primary \( \delta \) and vice versa. The alloys were found free from segregation with the exception of a thin surface layer, which was lower in tin content. These surface regions were carefully avoided or removed during specimen preparation. The alloys were not subjected to a long high temperature annealing treatment after rolling, for reasons discussed elsewhere.

Specimens for each kind of experiment were obtained from these bars using methods indicated in the respective sections below.
SECTION II  The design and development of the apparatus

A. The isothermal treatment apparatus

Previous work and initial experiments indicated that these alloys transformed very rapidly and that this apparatus should be capable of transferring several specimens simultaneously from a soaking bath to an isothermal bath, very quickly and consistently, and from there be capable of very rapid individual quenching.

The apparatus was therefore designed (Fig. 2.1) so that, after soaking, six specimens were transferred by a radial movement to the isothermal bath from where each could be quenched individually into water again using a radial pivot. The distance the specimens travelled through air was kept to a minimum. To ensure that the specimens once in the isothermal bath attained its temperature as rapidly as possible, lead, with its high heat capacity and conductivity, was used as the heating medium. However, although it was tried initially, lead proved unsuitable for the soaking bath as it dissolves the specimens rapidly at 700°C and above. Therefore, an air bath was constructed of chromized mild steel with individual recesses for each specimen. The specimens were always arranged to touch the surface of the block at the bottom of each recess.

The heating elements were constructed by threading 20 s.w.g. Nichrome wire through slots cut in sheets of SandanYo boarding so that all the wire was on the side close to the heating bath. The SandanYo sheets were then placed on five sides of the baths.
FIG. 2.1 DETAILS OF CONSTRUCTION
Fig. 2.1. The Isothermal Transformation apparatus
and each element connected in series. The wires were then insulated from the baths by sheets of amber mica.

Full details of apparatus construction are shown in Fig.2.1.

As the design of the air bath did not allow for direct 'side-ways' quenching into water, an additional shallow water bath was constructed to fit into the top of the cold lead bath for use when direct water quenching was required.

i. The Control of temperature

The temperature of both baths was controlled using Kent on/off recorder controllers in conjunction with variacs and chromel alumel thermocouples. The high temperature air bath was maintained to within $\pm 1^\circ C$ by using one thermocouple close to the windings to control temperature and another in the bath for temperature measurement. The temperature measured touching the bottom of each compartment did not vary by more than $1^\circ C$ from the observed temperature. The lower temperature lead bath was controlled and measured to within $\pm 2^\circ C$. by one thermocouple situated in the bath but as specimens were only in this bath for a relatively short time, this was considered adequate. The whole control system was designed to be flexible allowing frequent temperature checks to be made with a potentiometer and other furnaces to be connected into the system as necessary.
The cooling rates of specimens during isothermal transformation.

As these alloys transformed rapidly, it was considered important to know how quickly specimens reached bath temperature during transformation. The transfer and cooling rates for the apparatus were therefore obtained by casting a piece of 25% tin bronze around a fine insulated thermocouple wire. The cast bead was carefully filed down to specimen size, approximately $3/32$" cube, and then put through a cycle in the apparatus; except that the quench from the lead bath to water was performed manually and therefore was slower than normal. Concurrently, the temperature change was recorded on a Speedomax high speed recorder.

The cooling curves obtained showed the same basic shape, Fig. 2.2., and examples of the cooling rates are given in Table 2.2.

In the curve (Fig. 2.2.) $A - B$ represents the time of transfer and cooling rate on passing through air, $B - C$, the initial fast cooling rate on entering lead or water, and $C$ is the point of deviation from linearity as the cooling rate decreases on approaching the bath temperature at $D$.

On quenching from air to lead the cooling rate and time to reach temperature depended on the temperature differential of the quench, but the total time to reach isothermal temperature was always less than 2 seconds.

On water quenching the cooling rates did not vary greatly over the range considered and the specimens again reached the
Fig. 2.2. Sketch of the cooling curves obtained during isothermal transformation.

<table>
<thead>
<tr>
<th>Cooling Sequence</th>
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<tbody>
<tr>
<td></td>
<td>A</td>
<td>B</td>
<td>C</td>
<td>D</td>
<td></td>
</tr>
<tr>
<td>Total Time</td>
<td></td>
<td></td>
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<tr>
<td>Time to temp.</td>
<td></td>
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</table>

<table>
<thead>
<tr>
<th></th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
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</table>

Table 2.2. Examples of the cooling rates obtained during isothermal transformation.
water temperature in less than 2 seconds. The use of iced brine was found to offer no advantages in this instance as the high temperature microstructure could be retained unchanged.

The time to reach temperature on heating in the air bath was also measured and found to be less than 1 minute except for temperatures just above 520°C, when it took slightly longer due to the latent heat necessary for the \((\alpha + \delta) \rightarrow \gamma\) reaction to take place.

iii. Specimens

Individual specimens approximately 3/32" square were cut from the as received sheet and suspended in the baths by spot welding to nichrome wires.

E. The electrical resistivity apparatus

The apparatus used for the determination of electrical resistivity can be conveniently described in three parts:

i. The electrical measuring equipment, Figs. 2.3 and 2.4.

ii. The vacuum heating furnace for measurement at temperature Figs. 2.4 and 2.5.

iii. The vacuum quenching furnace for low temperature resistance measurements Figs. 2.6 and 2.7.

i. The electrical measuring equipment.

The potentiometric method of measuring resistance was decided upon as being the most accurate and convenient in this instance. It consists of passing a constant current through
the specimen and a standard resistance connected in series and measuring the potential drop across the specimen and standard by means of a potentiometer when a simple Ohm's Law calculation gives a resistance.

The problems of supplying a constant current were overcome by using a simple battery circuit giving an output of 2 volts. This consisted of a 12 volt 5 amp hour battery in parallel with two 2 volt cells also in parallel (Fig. 2.3). An ammeter and a variable resistance were also in the circuit and adjusted so that no current flowed round the battery circuit as indicated by the ammeter reading zero. By this means little change in current occurred over a period of a day.

The standard resistance was constructed of a fully annealed brass strip immersed in oil to prevent temperature fluctuations and calibrated for ambient temperature variations against a known standard resistance.

A Tinsley potentiometer and galvanometer were used; the potentiometer capable of measuring changes of one micro-volt and the galvanometer covering a full scale deflection of 22 microvolts.

All flow and return wires were run parallel to each other and all joints, both soldered and demountable, were adjacent so as to minimise any effects due to thermal e.m.f.'s. The current of approximately 1.5 amperes, was allowed to flow for sufficient time for the circuit to reach equilibrium temperature
The circuit for resistance measurement

Fig. 2.3.
before any readings were taken.

ii. The vacuum heating furnace for the measurement of resistance at temperature.

Full details of the vacuum heating furnace are shown in Figs. 2.4. and 2.5.

The furnace, which was pivoted at its centre to allow the specimen to be inserted into the vacuum tight mullite tube, was wound with Nichrome wire to give a constant temperature zone approximately 8" long. The heating rate of the furnace was controlled with a variac and a controller was used for constant temperature work as necessary. The mullite tube, which was connected to the pumping system by a demountable vacuum connector, was surrounded by an earthed ferritic stainless steel tube which acted as a temperature equaliser and protected the specimen from induced currents. The vacuum obtained was approximately $10^{-4}$ m.m. of mercury.

The current was carried to the specimen by nickel wires, which were connected to the specimen by copper screw connectors, while thin copper wires welded to the specimen were used to measure the potential difference. The temperature of the specimen was obtained by spot welding a thin chromel alumel thermocouple bead to the centre of the specimen. All the wires were inserted into the vacuum system by glass metal seals.

ii(a) The development of the measuring technique

During the development of this equipment, attempts were made
to make the resistance temperature measurement automatic.

Initially, a Graphispot spot-following galvanometer was used in place of the Tinsley galvanometer to record the e.m.f. changes and a Kent recorder to measure temperature. In order to utilise a sufficiently accurate scale on the galvanometer to observe the small changes taking place, a constant back e.m.f. was required to reduce the total magnitude of the measured e.m.f. without affecting the size of any change. This was introduced by partial balancing with the potentiometer. However, collation of the results from the two recorders was so tedious as to offer no net advantages for this method.

Attempts were also made to use a Speedomax X-Y recorder to measure e.m.f. versus temperature directly; in this case a back e.m.f. was required for both ordinates. Thus there were five sources of e.m.f. which needed standardisation and the inevitable complication and loss in accuracy which resulted, were not justified.

Therefore apart from a few curves, all results were obtained manually.

ii(b) Investigation of the temperature gradient existing in the specimen.

To investigate the possibility of a temperature gradient existing along the specimen, chromel-alumel thermocouples were welded to the specimen at each end. It was thought that the potential difference could also be obtained by measuring the e.m.f. from either the two alumel of the two chromal wires.
With the current off, the temperature gradient was found to be less than 2°C, but immediately on switching on the measuring current, the gradient appeared to be 30-40°C. However, the potential difference as determined by the chromel or alumel wires also differed by an amount equivalent to this temperature difference.

The reason for this was difficult to locate. The heating and cooling of the respective junctions due to the Peltier effect was considered but as heating effects take time to materialise and this change appeared immediately, this was thought unlikely.

It was also considered that the individual wires of each thermocouple might not be welded to the specimen at identical positions as illustrated in Fig. 2.8. If this were the case, the different potentials measured would correspond to the different lengths and this would also effect one or both temperatures. In the example shown (Fig. 2.8.) T₁ would represent the true temperature and T₂ would be the true temperature less the potential drop from (3) to (2). On reversing the current, T₁ should remain constant and T₂ should now be T+P.D. but in fact, the temperatures were reversed both in magnitude and position; a situation which could only occur if there were the same misalignment at both thermocouples. The potential differences measured by the chromel and alumel respectively, were also reversed.

It appeared that oxide on one or both of the thermocouples was causing some partial rectification and by carefully cleaning the
**Schematic diagram of the problem encountered during the determination of the temperature gradient along resistivity specimen - see text.**
wires before spot welding, it was found possible to remove the
effect.

It was concluded that the temperature gradient along the
specimen did not exceed 2°C.

For subsequent experiments copper wires were used to measure
the potential drop and the temperature was obtained from a thermo-
couple welded to the centre of the specimen. The thermocouple
was checked each time after mounting to see if the measuring
current affected its temperature reading.

iii. The vacuum quenching furnace for low temperature resistivity
measurements.

Vacuum heating and quenching of specimens was performed in
the apparatus shown in Figs. 2.6. and 2.7. The technique for
the heat treatment of a specimen was as follows:

The furnace was heated to the desired temperature and the
specimen inserted into the top cold part of the silica tube which
was then backed down to a suitable vacuum (less than 10 microns
proved satisfactory) then the specimen was dropped into the hot
zone of the furnace. During this time the magnetic valve (1)
(Fig. 2.7.) sealed the system and valve (2) connected the system
to the backing train. After the prescribed heat treatment the
apparatus was prepared for water quenching by removing the screw
cap from (X), inserting the end of tube (A) below the surface of
water in a container, connecting an argon supply at 10 lbs. per sq.
in. to (4) and closing the baffle valve on the diffusion pump.
Control chromel alumel thermocouple

Silica tube

Measuring thermocouple

Specimen

Furnace

Magnetic Valve 1.

Magnetic Valve 2.

Argon Supply 4

To Diffusion pump.

Demountable joint Y

Demountable joint X

Water level during quenching

Fig. 2.7. Arrangement for vacuum heat-treatment and quenching.
Fig. 2.6. The Apparatus for vacuum heat-treatment and quenching
By pressing the micro-switch, which opened valve (1) and closed valve (2), the system was flooded with argon which allowed cap (X) to fall off and the specimen was dropped into the water. The pipe under the water level was disconnected at (Y) before releasing the micro-switch to prevent the water sucking back.

The specimens were freely suspended in the furnace by clamping to a wire with a mild steel screw clamp. Suspension and release was by a simple slot and groove arrangement so that when the specimen was dropped into the hot zone, it slid, with its holder, down another wire which had a stop at the centre of the furnace.

Initially, a thin perforated copper tube was used to contain the specimen as it was thought that distortion might occur during quenching. These fears were unfounded but the copper tube did pick up tin from the vapour and hence from the specimen. This resulted in a far greater tin loss from the specimen than was expected and hence a continuously decreasing resistance.

The temperature was controlled by a Kent on/off controller recorder by a thermocouple situated between the furnace tube and the silica tube and measured by another thermocouple inside the silica tube at the same level as the specimen.

The resistance after quenching was measured using the same electrical apparatus as for the high temperature work except that the specimen together with a stirrer and an alcohol thermometer were inserted into a beaker of alcohol (Fig. 2.9). This beaker was surrounded by another into which liquid air was poured to
Fig. 2.9. The arrangement for low temperature resistivity measurements.
cool the specimen and hence obtain the temperature coefficient of resistance. The stirring action was sufficient to prevent a temperature gradient along the specimen.

iv. Specimens

Specimens for all the resistivity measurements were cut from the as received bars then filed and polished in a small jig until they were approximately 1 m.m. square and 5 c.m. long. The bars were required in as ductile condition as possible for this operation and to facilitate this they were heated for a short time at a low temperature just inside the ρcY region and quenched.

The probes of copper wire were connected to the specimens by spot welding for all the high temperature and some low temperature resistivity measurements and also, for the other low temperature measurements, by clamping the specimens, after heat treatment, to a jig on to which two probes were fixed. For the low temperature work the welding of the probes, which were heat treated in situ, ensured that successive measurements after repeated quenching included exactly the same volume of specimen and any slight distortion was not important. However, if successive heat treatments were performed at a high temperature, diffusion of tin "down" the copper probes occurred resulting in a slight decrease in resistance. On the other hand while clamping prevented contamination of the specimens, minor distortion and differences in volume of the specimen along its length caused erroneous results.
The specimens were made this way largely to be of identical material to that used for the other experiments. Of the other methods available, casting was unsuitable because of the possibility of segregation and porosity. Extrusion was briefly tried but was unsuccessful although the method was not thought impossible with these alloys. Powder metallurgy was not tried but might be useful as compacted long lengths could be constructed similar to those machined in iron aluminium alloys by Cahn and Feder\textsuperscript{45}.

The specimens were small and, therefore, so were the resulting e.m.f.'s but this was not a serious problem. The major obstacle to accurate resistivity measurements was the volume determination. Two methods were tried:

(a) The measurement of area at six positions along the length of the specimen using a micrometer.
(b) The determination of volume by Archimedes' Principle.

Repeated measurements on two specimens after successive heat treatments and quenching resulted in the variation of 2\% and 3\% respectively by method (a) and 5\% by method (b) but the results by method (b) were, on average, 7\% lower than those obtained by method (a). Both methods are open to criticism; (a) because it always measured the largest possible width; (b) because of the small weight loss noted, because of bubble occlusion and because it included the ends of the specimen outside the probe length which were invariably thinner than the rest of the specimen. In
view of these results method (a) was adopted as the more consistent and it was concluded that:

(a) changes on individual specimens of the order of ± 0.1% could be measured and because of this, if several specimens of the same composition were compared, the results were always normalised to a datum position where the resistivities were considered equal.

(b) Values of specific resistance when compared with others obtained in this research are accurate to within ± 3%.

(c) Absolute values of specific resistance for general comparison may be up to 10% too high.

C. The X-ray equipment.

X-ray diffraction photographs with specimens quenched from the vacuum quenching furnace (Fig. 2.7) were taken in the following cameras:

(a) A Phillips 57.54 m.m. powder camera for the identification of lines with moderate accuracy of measurement.

(b) A Phillips 114.03 m.m. powder camera to obtain a higher accuracy during the determination of the lattice parameters.

The high temperature X-ray photographs were obtained in a 19 c.m. Unicam high temperature camera.

In all cases nickel filtered copper radiation was used.

1. Specimens

Block powder specimens were made by preparing 1 m.m. square rods as for the resistivity experiments and then polishing these down to ½ m.m. diameter rod with coarse emery paper in a high speed
Unfortunately, and unexpectedly in view of the manufacturing procedure, the bars as supplied had a grain size of about \( \frac{1}{4} \) m.m. diameter so that powder photographs were far from ideal, being rather spotted. This made photometer intensity measurements impossible and optical comparison difficult. It was not possible to overcome this as grain refinement of these materials does not occur during the eutectoid reaction as it does in the case of steels.
CHAPTER III
THE EXPERIMENTAL RESULTS I
THE binary COPPER-TIN ALLOYS

SECTION 1 The electrical resistivity results

A Measurements obtained at elevated temperatures

The apparent electrical resistivity temperature curves obtained for the 23.3\%, 25.7\%, 27.5\% and 29.2\% tin alloys are shown in Figs. 3.1 to 3.5. All of these alloys were in the as hot rolled condition as described in Chapter II unless otherwise stated. The respective heating and cooling rates quoted are the average values used for the temperature range from 500°C to the maximum temperature utilised unless it is stated otherwise. The curves all have the same basic features which will now be described:

(i) The resistance change associated with the eutectoid reaction 
\[ \alpha + \delta \rightarrow \gamma \]

On heating through the eutectoid reaction, there is a large decrease in resistance which increases with increasing tin content and therefore with the percentage of \( \delta \) in the microstructure. The reverse change occurs on cooling with a hysteresis of about 20°C, which varies slightly with the cooling rates used. The resistance of the \( \alpha+\delta \) mixture after cooling is invariably lower than it was on heating but this is probably due to the different distribution of \( \alpha \) and \( \delta \); although in some alloys the proportions of \( \alpha \) and \( \delta \) may vary as indicated by the isothermal transformation experiments.
Resistivity Curves of tin alloy - Fig. 3.1

Heat Treatment Cycle

<table>
<thead>
<tr>
<th>Heating Rate</th>
<th>Time at Temp.</th>
<th>Cooling Rate</th>
</tr>
</thead>
<tbody>
<tr>
<td>X2, 2°C/min.</td>
<td>-</td>
<td>03°C/min.</td>
</tr>
<tr>
<td>9°C/min.</td>
<td>to 750°C.</td>
<td>6°C/min.</td>
</tr>
<tr>
<td>to 772°C.</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Melting occurred.
Resistivity Curves 25% tin alloy - Fig. 3.2

Heat Treatment Cycle

<table>
<thead>
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<th>Heating Rate</th>
<th>Time at Temp.</th>
<th>Cooling Rate</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>× 2.1°C/min</td>
<td>160 mins. 740°C</td>
<td>× 0.2°C/min</td>
</tr>
<tr>
<td>2</td>
<td>× 0.96°C/min</td>
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</tbody>
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*Values normalised to value of Specimen 1 at 700°C. for comparison.*
Resistivity Curves 26% tin alloy - Fig. 3.3

<table>
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<td>Specimen</td>
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<tr>
<td>2</td>
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<td></td>
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Melting occurred

Resistivity Micro-Ohms / cm$^2$

Temperature $^\circ C.$
Heat Treatment Cycle

<table>
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<th>Heating Rate</th>
<th>Time at Temp</th>
<th>Cooling Rate</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.6°C/min</td>
<td>30 mins</td>
<td>6.6°C/min</td>
</tr>
<tr>
<td>2</td>
<td>2.4°C/min</td>
<td>135 mins</td>
<td>1.7°C/min</td>
</tr>
</tbody>
</table>

*Previously heated for 2 hours at 730°C.
Resistivity Curves 25% tin alloy - Fig. 3.5.

<table>
<thead>
<tr>
<th>Heating rate</th>
<th>Time at</th>
<th>Cooling rate</th>
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<tbody>
<tr>
<td>1.9°C/min.</td>
<td>60 mins</td>
<td>2°C/min.</td>
</tr>
<tr>
<td>710°C</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Heat Treatment Cycle

Resistivity Micro-ohms / cm.³

450°C 500°C 550°C 600°C 650°C 700°C 750°C 800°C
(ii) The resistance change due to the solution of the primary phase.

(a) Hypoeutectoid Alloys

As $\alpha$ dissolves in $\beta$ with the increasing temperature there is a small increase in resistance which is observed as a decrease in the slope of the resistance-temperature curve. This change occurs irrespective of the final solution temperature. Thus, for the 23% alloy there is an inflection in the curve at the 586°C arrest due to the extra amount of $\alpha$ dissolved and a further slope change of the same form at 726°C as the last of the dissolves. The remaining hypoeutectoid alloys have only one inflection as all the $\alpha$ dissolves at or below 586°C.

(b) Hypoalloy Alloys

The solution of primary $\delta$ in $\beta$ on heating causes a further large decrease in the resistance of the alloy in addition to the decrease caused by the eutectoid reaction.

(iii) The apparent resistivity-temperature curves in the $\gamma$ phase field

All of the resistance-temperature curves obtained by heating and cooling through the $\gamma$ region are smooth without any inflection points or irregularities but there is a general increase in the temperature coefficient of electrical resistivity with increasing temperature. This variation of temperature coefficient for each alloy is shown in Table 3.1. These were obtained by constructing tangents to the resistivity-temperature curves at the temperatures indicated and show that the temperature coefficient increases with increasing tin content to a maximum of 27% tin and then decreases again. The values for the 27% tin alloy also increase with
**TABLE 3.1.**

The temperature coefficients (micro-ohms/cm²/100°C) of resistivity of the binary alloys.

(obtained by constructing tangents to the resistivity temperature curves at the temperature shown)
temperature more than the other alloys. Some alloys (Fig. 3.1. and 3.3.) were heated until melting began and the results obtained used to supplement the metallography determination of the solidus (Section II).

(a) The effect of varying the heating and cooling rates.

The heating and cooling rates used for these curves varied between 0.5 and 9°C. per minute and this variation caused only minor variations in the heating and cooling curves as would be expected from hysteresis effects. Thus cooling curves diverged from heating curves at lower temperatures if the cooling rates used were greater than approximately 2°C./min. e.g. (Figs. 3.2, 3.4, and 3.5) while the faster heating rates caused the curves to be straighter at low temperatures although they agreed at higher temperatures e.g. (Fig. 3.2.) indicating that the low temperature equilibrium resistivity values may be slightly higher than shown here.

(b) The effect of holding at a high temperature

The 25%, 26%, 27%, and 28% tin alloys were held at a temperature approximately 30°C. below their melting points for a minimum period of 30 minutes following slow heating and prior to cooling. During this annealing, the resistivity of the 26% and 27% tin alloys decreased by approximately 0.25 micro-ohms per cm.³ and 0.35 micro-ohms per cm.³ respectively but there was no change in the resistivity of the 25% and 28% tin alloys although they were annealed for longer times.
Fig. 3.6. The variation of resistivity with composition at constant temps.
than were necessary to cause the decrease in the other alloys. The decrease in 26\% and 27\% tin alloys was maintained on cooling and on reheating (Fig. 3.3. and 3.4.) although there was some discrepancy at low temperatures due to the cooling rates used (Fig. 3.4.).

If these specimens were annealed prior to heating (Specimen 2 Fig. 3.4.) then the decrease was not observed.

iv. Resistivity Composition Curves

The variations of resistivity with composition at constant temperature, are shown in Fig. 3.6. The values plotted are means of those obtained and the deviations indicate the probable errors as discussed in Chapter II. It can be seen that while the resistivity of the \((\alpha + \delta)\) and \((\alpha + \beta)\) structures increase continually with tin content the resistivity of \(\beta\) does not, particularly at higher temperatures.

B. The resistivity of quenched specimens

The specimens for these experiments were constructed from material in the same condition as that used for the high temperature experiments and then the room temperature resistance was measured after three differing heat treatment procedures. These are shown schematically in Fig. 3.7. and are studies of:-

(i) The effect of time at high temperature

Individual alloys were repeatedly annealed for varying times at a constant temperature, quenched and the resistivity measured after each anneal. These experiments were used to investigate
Fig. 3.7. The heating cycles used during the heat treatment of low temperature resistivity specimens.
the possibility of a decrease in the room temperature resistance similar to that observed in some alloys during high temperature resistivity measurements. Although quenching retains the high temperature structure as observed microscopically the two techniques are not directly comparable because during subsequent reheating the retained structure certainly decomposes and then has to be redissolved.

(i) The effect of increasing annealing temperature on the as prepared samples.

These results combine the effect of temperature on the resistance with the effect of high temperature annealing as investigated under section (i).

(iii) The resistance-temperature curve

The results were determined after annealing to remove any of the effect observed in section (i).

In all these experiments the resistance was measured directly after quenching. The effect of ageing at room temperature was also briefly investigated and the results are reported.

As there were no marked changes in the room temperature resistance of these alloys, only some typical results are reported.

(i) The effect of time at high temperature

The effect of time at temperature on the 25% and 26% tin alloys at 750°C and 700°C, respectively, are shown in Fig. 3.8. The temperature coefficient at 0°C is also plotted on this figure as a sloping line which represents the variation in resistivity from +20°C to -20°C. Both curves indicate a decrease
Fig. 3.8. The effect of time at temperature on the low temperature resistivity
in resistivity which reaches a minimum after approximately 90 minutes and then returns to its original value. However, thereafter the results for the 25% tin alloy show some scatter while those for the 26% tin alloy are constant. The minimum in the 26% tin alloy is also associated with a small change in the temperature coefficient of resistance which is not evident for the 25% tin alloy. This and the scatter observed, cast some doubt on the validity of the minimum in the 25% tin alloy.

ii. The effect of increasing the annealing temperature on the as prepared samples.

The effect of increased annealing temperature on the room temperature resistivity of the 25%, 26% and 27% tin alloys is shown in Fig. 3.9. It indicates that the room temperature resistivity of the 25% tin alloy is independent of annealing temperature while the resistivity of the 26% and 27% tin alloys pass through a minimum with increasing temperature. The decrease in resistance of the 26% alloy is of similar magnitude to the decrease observed during isothermal annealing (Fig. 3.8).

iii. The resistivity temperature curves

The resistivity temperature curves of the 25% and 26% tin alloys are shown in Fig. 3.10. These indicate that the resistance of the 25% tin alloy is still independent of temperature while the resistance of the 26% tin alloy is also largely independent of temperature except at 600°C.
Fig. 3.9. The effect of increasing annealing temperature on the resistivity at 0°C. (15 mins. at each temperature.)

- Resistivity measured at 0°C.
- Dashed sloping line shows temperature coefficient from -20°C. to +20°C.
iv. The effect of room temperature ageing on the resistivity of the 25 tin alloy.

On ageing the 25% tin alloy at room temperature, no change was observed after four hours but after 16 hours an increase was observed as shown in Fig. 3.10, which was independent of quenching temperature.
Fig. 3.10. Low temperature resistivity-curves.

- Resistivity measured at 0°C.
- Dashed sloping line shows temperature coefficient from -20°C to +20°C.
- Resistivity measured at 0°C after ageing at room temperature for 16 hrs.
SECTION II  Metallographic Examination of the heat treated alloys

A. The determination of the solidus curve for alloys containing from 22.7 - 28.7 tin.

To clarify the nature of the reaction which occurs at 755°C during the solidification of alloys containing from 27.3 - 30.5 tin, the solidus temperature in this region was determined.

Specimens were heated in the isothermal transformation apparatus, at increasing temperature, for a minimum time of one hour then water quenched and examined microscopically. The presence of any liquid phase which was present prior to quenching is readily detected in the microstructure where it occurs either as 'pools' or as a discontinuous grain boundary network of tin rich γ or δ. δ was often present because β of high tin content is very difficult to retain by quenching.

The liquidus curve was determined by bracketing the results which are shown in Fig. 3.11. Some melting temperatures obtained from resistivity curves were also used to supplement these results.

B. The determination of the isothermal transformation curves.

Isothermal transformation experiments were performed on a range of alloys whose composition extended across the (β + γ) field (Fig.1.1) from 25.5 to 28.5 tin. As indicated earlier, the alloys were transformed in the (α + δ) region (350 to 520°C) after annealing at various temperatures in the β and γ phase fields. The annealing temperatures used were the maximum and minimum at which a homogeneous β or γ phase could reasonably
Fig. 3.11. Liquidus curve determined as a result of quenching experiments and resistance results - currently accepted results shown dotted.
Fig. 3.13. 25% Tin Alloy Time-Temperature Transformation Curve.

Specimens annealed for 60 mins. at 700°C. Similar results obtained after annealing at 750°C, 650°C and 600°C.
Fig. 3.15 26% tin alloy Time Temperature Transformation Curve
Specimens annealed for 90 mins. at 740°C.
Fig. 3.16. 27% tin-allow. Temperature-Transformation Curve.
Specimens annealed for 90 mins. at 570°C.
Fig. 3.17 27% tin alloy time-temperature transformation curve

Specimens annealed for 90 mins. at 730°C.
Fig. 3.18 28% tin alloy. Time-temperature transformation curve. 
Specimens annealed for 90 mins. at 735°C or 90 mins. at 575°C.
be expected to exist.

The isothermal transformation curves obtained for these alloys after the annealing treatments indicated are shown in Fig.3.13 to Fig. 3.18. The curves were determined by examination of the microstructures using optical estimations of the percentage transformed and bracketing of the results to determine the start and finish lines.

(i) The transformation characteristics of the $\beta$ phase.

The transformation characteristics of these alloys follow a general pattern which varies for each individual alloy according to its composition and for certain alloys, the annealing temperature.

The Hypoeutectoid Alloys

(a) The morphology of primary $\alpha$ precipitation

For all hypoeutectoid alloys, primary $\alpha$ precipitates within the grains at temperatures above the eutectoid temperature of 520°C. At temperatures just below the $\beta/(\alpha+\beta)$ boundaries for the particular alloy, $\alpha$ precipitates as broad needles which are nucleated randomly within the $\beta$ structure. Associated with this precipitate there is a formation of sub-grains probably due to the stresses involved and a darkening of the surrounding $\beta$ because of local tin enrichment, Fig.3.12. The size and shape of the sub-grains are related to the local areas of $\alpha$, i.e. needles of $\alpha$ result in elongated sub-grains while rounder $\alpha$ precipitates are associated with equi-axed sub-grains.
25% tin alloy annealed at 700°C and transformed for 1800 secs. at 560°C.

Structure Primary α (light) precipitation in a matrix of β which shows sub-graining.

Fig. 3.12. x 135

25% tin alloy annealed at 700°C and transformed for 120 secs. at 525°C.

Structure Colonies of primary α precipitating in a matrix of β

All specimens polished mechanically and etched in alcoholic ferric chloride.
As the transformation temperature decreases, the $\alpha$ forms at the $\beta$ grain boundaries and as colonies of Widmanstätten precipitate which usually grow close to but away from the grain boundary precipitate Fig. 3.19. The $\alpha$ is finer and is still associated with the sub-grains which are also finer and therefore more difficult to detect.

(b) The eutectoid reaction

Below the eutectoid temperature, the $\alpha$ forms in a similar manner (Fig. 3.20) and in addition, after longer time, $\delta$ nucleates on and surrounding the particles of $\alpha$ (Fig. 3.21). The $\delta$ also forms at and around the prior $\beta$ grain boundaries at first (Fig. 3.20). The reaction continues by more $\alpha$ precipitation nucleating further and so on until the reaction is complete. Except in a few isolated cases in the 27% tin alloy where a lamella eutectoid is sometimes formed, initially there is not a genuine pearlitic eutectoid in these alloys, each phase forms independently of the other, the reaction being really of a bainitic nature. Thus, the eutectoid start in the 'S' curves could equally well be interpreted as the start of the second phase. As the transformation temperature is lowered the lead of the primary $\alpha$ decreases and eventually disappears so that both phases nucleate simultaneously. In alloys close to the eutectoid composition, primary $\delta$ rosettes occur at still lower temperatures. The structure becomes finer but the eutectoid morphology remains unchanged (Fig. 3.22). However, the sites of nucleation and the growth form of the eutectoid do vary.
Fig. 3.20
25% tin alloy annealed at 750°C and transformed
for 60 secs. at 500°C.
Structure Primary α (light) in a matrix of β with eutectoid
(dark) forming from the prior β grain boundaries.

Fig. 3.21
27% tin alloy annealed at 730°C and transformed
for 4760 secs. at 517°C.
Structure Primary α (light) surrounded by δ forming the
typical eutectoid structure in a matrix of β.
Fig. 3.22
25% tin alloy annealed at 700°C and transformed for 60 secs. at 475°C.

Structure Fine eutectoid of α surrounded by δ in a matrix of β.

Fig. 3.23
25% tin alloy annealed at 700°C and transformed for 30 secs. at 450°C.

Structure Widmannstätten eutectoid forming from the prior β grain boundaries and within the β grain.
considerably over a small temperature range and may take the following forms:

(c) **The Widmannstatten eutectoid**

At temperatures just above those at which primary α ceases to form, the eutectoid grows from the prior β grain boundaries and as needle-shaped eutectoid within the grains (Fig. 3.23). These needles become more lenticular as the temperature is lowered.

(d) **The grain boundary eutectoid**

Eventually the intergranular Widmannstatten eutectoid ceases to occur and the reaction is completed solely by growth from the prior β grain boundaries Fig. 3.24.

(e) **The cuboidal precipitate**

At lower temperatures still, precipitation recurs within the grains and this time takes the form of cuboids of eutectoid which are believed to be nucleated by δ (Fig. 3.25). This intergranular nucleation, which initially occurs only in sparsely, becomes a predominant form of growth at slightly lower temperatures.

(f) **The formation of δ as a second primary phase.**

Although all these forms of eutectoid are observed in the lower tin alloys, some alloys of composition closer to the eutectoid form δ as a definite primary phase; although their composition is nominally hypoeutectoid. When primary δ occurs, it does so in the characteristic γ brass rosette pattern, both at the β grain boundaries and homogeneously over the grains. However, it does not radically affect the form of the eutectoid which follows it and
Fig. 3.24.  x 80
25% tin alloy annealed at 700°C. and transformed for 40 secs. at 443°C.
Structure  Eutectoid forming solely from the prior $\beta$ grain boundaries.

Fig. 3.25.  x 80
25% tin alloy annealed at 700°C. and transformed for 5 secs. at 398°C.
Structure  Grain boundary eutectoid and cuboids of eutectoid forming within the $\beta$ grains.
which tends to grow irrespective of the $\delta$ nuclei. Thus the eutectoid initially grows solely from the prior $\beta$ boundaries (Fig. 3.26) while at lower temperatures intergranular cuboidal growth also takes place (Fig. 3.27).

**Hypereutectoid alloys**

(a) The morphology of primary $\delta$.

In these alloys the precipitation of primary $\delta$ is very difficult to suppress. It forms very rapidly both above and just below the eutectoid as a grain boundary and intergranular precipitate on many nucleation sites (Fig. 3.28), some of which initially grow to a cuboidal form. However, these nuclei rapidly spheroidize and decrease in number to form a remarkable stable structure of $(\delta + \beta)$ (Fig. 3.29) although massive $\delta$ may occur in some grains.

(b) The eutectoid reaction

At temperatures just below the eutectoid temperature there is a considerable delay before eutectoid formation occurs in a similar manner to the hypoeutectoid alloys, i.e. needles of $\delta$ form and the $\delta$ 'accumulates' around these needles (Fig. 3.30). The resultant structure is very difficult to recognize as hypereutectoid.

At temperatures below a proximately 2000°C, the structures are similar to the hypoeutectoid alloys in which primary $\delta$ forms. The $\delta$ forms as a grain boundary and intergranular rosette type precipitate and the eutectoid subsequently forms from the prior $\beta$ boundaries (Fig. 3.31).
Fig. 3.26. 27% tin alloy annealed at 550°C and transformed for 60 secs. at 494°C.

Structure  Primary $\delta$ forming at the prior $\beta$ boundaries and as rosettes within the $\beta$ grains with eutectoid (dark) beginning to form.

Fig. 3.27. 27% tin alloy annealed at 730°C and transformed for 30 secs. at 424°C.

Structure  Primary $\delta$ rosettes and eutectoid forming from the prior $\beta$ boundaries and as cuboids within the $\beta$ grains.
28% tin alloy annealed at 735°C and transformed for 3 secs. at 505°C.

**Structure** Primary δ forming at the prior β grain boundaries, as cuboids and as many nuclei within the β grains.

28% tin alloy annealed at 735°C and transformed for 840 secs. at 505°C.

**Structure** Primary δ spheroidised as a result of holding at 505°C.
Structure: Typical eutectoid of \( \alpha \) surrounded by \( \delta \) formed from \( \gamma \) grain boundaries.

Fig. 3.31

28\% tin alloy annealed at 735\(^\circ\)C and transformed for 2700 secs. at 505\(^\circ\)C.

Structure: Unresolved precipitation of primary \( \delta \) (dark) with eutectoid forming from the prior \( \gamma \) grain boundaries.
(ii) **The transformation product below 400°C**

During the transformation of both the hypo and hyper eutectoid alloy below 400°C, there is a marked change in the slope of the finish curve indicating a change in the reaction rate. In association with this change a light etching phase appears in the microstructure which, initially, is dispersed within and takes the morphology of the \((\alpha+\delta)\) eutectoid. (Fig.3.32). However, at temperatures around 350°C, this featureless phase which will be designated \(\beta^*\) has almost completely replaced the \((\alpha+\delta)\) eutectoid as the decomposition product (Fig.3.33).

(iii) **The effect of the annealing temperature on the transformation product**

The variation of the annealing temperatures within the experimental conditions tried had no effect on the transformation product of the 25% and 22% tin alloys.

The transformation product of the 26% and 27% tin alloys does, however, depend on the prior annealing temperature and the differences between the products are illustrated by the 'S' curves Figs.3.14 to 3.17 and may be summarised as follows:

**The 26% tin alloy.**

The high temperature annealing favours the formation of \(\alpha\) which nucleates sooner and as primary to a lower isothermal temperature, while primary \(\delta\) does not form at any isothermal temperature. After the low temperature anneal \(\alpha\) only forms
Fig. 3.32  
25% tin alloy annealed at 700°C and transformed for 30 secs. at 383°C.

Structure: Eutectoid forming from the β grain boundaries and as cuboids with the additional light phase β* forming within the eutectoid.

Fig. 3.33  
27% tin alloy annealed at 730°C and transformed for 5 secs. at 354°C.

Structure: Alloy almost completely transformed from β to β*.
over a small range at high isothermal temperatures and \( \gamma \) occurs as primary phase below approximately 475°C. Figs. 3.34 to 3.37 show the difference between the structures occurring at 485°C and 425°C, respectively.

The 27\% tin alloy

After the high temperature annealing primary\( \alpha \) forms down to 505°C, eutectoid only from 505°C to 460°C, and primary \( \delta \) plus eutectoid below 460°C. The low temperature anneal favours the formation of primary \( \delta \) which occurs at all temperatures from 505°C downwards with only a very limited amount of primary \( \alpha \) at 520°C. Figs. 3.38 and 3.39 indicate the difference between the two microstructures on transforming at 485°C.

(iv) Factors affecting the type of transformation product.

In view of the considerable differences between the curves obtained for the 26\% and 27\% tin alloys after varying annealing temperatures, further experiments were carried out to determine the factors controlling the formation of either curve. A constant isothermal temperature which showed the most obvious difference in transformation product, was selected for each alloy and the structure obtained on transforming at this temperature used as the criterion to decide which curve would be formed. The temperatures chosen were 400°C for the 26\% tin alloy and 495°C for the 27\% alloy and using these as the isothermal temperatures the following experiments were carried out:
Fig. 3.34  x 210
26% tin alloy - Annealed 740°C
Transformed 30 secs. at 487°C.
Structure  Primary α + eutectoid and β

Fig. 3.35  x 210
26% tin alloy - Annealed 580°C.
Transformed 30 secs. at 485°C.
Structure  Eutectoid and β

Fig. 3.36  x 210
26% tin alloy - Annealed 740°C
Transformed 10 secs. at 422°C.
Structure  Eutectoid and β

Fig. 3.37  x 620
26% tin alloy - Annealed 580°C
Transformed 20 secs. at 421°C
Structure  Primary α + eutectoid and β
Fig. 3.38  x 210
27% tin alloy - Annealed 720°C.
Transformed 60 secs. at 484°C
Structure: Widmannstätten
eutectoid and β

Fig. 3.39  x 200
27% tin alloy - Annealed 570°C.
Transformed 60 secs. at 484°C
Structure: Primary β rosettes,
eutectoid and β
(a) Specimens were annealed at lower temperatures in the \( \beta / \gamma \) region following the high temperature annealing (a) treatment in an attempt to reform the low temperature structure.

(b) Following a high temperature anneal and transformation, specimens were re-annealed at lower temperatures in the \( \beta / \gamma \) region and re-transformed.

(c) Following a low temperature anneal (b) and transformation, specimens were re-annealed at high temperature in the \( \beta / \gamma \) region and re-transformed.

(d) Specimens were annealed for varying times at soaking temperatures intermediate to those used for the basic curves.

The results of experiments (a), (b) and (c) which are summarised in Table 3.2., indicate that whilst the high temperature structure could be formed after the low temperature structure by re-treating at a high soaking temperature, the reverse was not possible. The high temperature structure once formed was found to be stable whatever the subsequent heat treatment used.

Experiment (d) showed that the change in transformation product was a time temperature relationship. If log time is plotted against the type of transformation products for the two alloys

\[ \beta_{LT}^{(a')} \text{ 90 mins. at } 740^\circ C \text{, for the } 26.5 \text{ tin alloy or 90 mins. at } 735^\circ C \text{ for the } 27.5 \text{ tin alloy.} \]

\[ \beta_{LT}^{(b')} \text{ 90 mins. at } 560^\circ C \text{, for the } 26.5 \text{ tin alloy or 90 mins. at } 570^\circ C \text{ for the } 27.5 \text{ tin alloy.} \]
The effect of heat treatment on the type of isothermal transformation product in the 27% tin alloy

<table>
<thead>
<tr>
<th>Soaking Temperature</th>
<th>Soaking Time (Hrs.)</th>
<th>Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>700°C</td>
<td>3</td>
<td>Eutectoid $\alpha + \gamma$ corresponds to 730°C. curve</td>
</tr>
<tr>
<td>700°C</td>
<td>1</td>
<td>Eutectoid $\alpha + \gamma$ with a few areas of primary</td>
</tr>
<tr>
<td>700°C</td>
<td>1</td>
<td>Eutectoid $\alpha + \gamma$ with a few areas of primary</td>
</tr>
<tr>
<td>672°C</td>
<td>1</td>
<td>Eutectoid $\alpha + \gamma$ with a few areas of primary</td>
</tr>
<tr>
<td>660°C</td>
<td>$\frac{1}{2}$</td>
<td>Eutectoid $\alpha + \gamma$ with a few areas of primary</td>
</tr>
<tr>
<td>650°C</td>
<td>$\frac{1}{4}$</td>
<td>Eutectoid $\alpha + \gamma$ with a few areas of primary</td>
</tr>
<tr>
<td>649°C</td>
<td>1</td>
<td>Primary $\gamma$ and $(\alpha + \gamma)$ eutectoid corresponding to 570°C. curve</td>
</tr>
<tr>
<td>645°C</td>
<td>1</td>
<td>Eutectoid $\alpha + \gamma$ with a few areas of primary</td>
</tr>
<tr>
<td>600°C</td>
<td>1</td>
<td>Eutectoid $\alpha + \gamma$ with a few areas of primary</td>
</tr>
<tr>
<td>570°C</td>
<td>2</td>
<td>Eutectoid $\alpha + \gamma$ with a few areas of primary</td>
</tr>
<tr>
<td>568°C + 4°C</td>
<td>17</td>
<td>Eutectoid $\alpha + \gamma$ with a few areas of primary</td>
</tr>
</tbody>
</table>

The structure after heating at 730°C for 90 minutes, furnace cooling to temperature shown and holding for time indicated then transforming at 495°C

<table>
<thead>
<tr>
<th>Soaking Temperature</th>
<th>Time at Temperature (Hrs.)</th>
<th>Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>650°C</td>
<td>1</td>
<td>Eutectoid $\alpha + \gamma$ corresponding to 730°C. curve</td>
</tr>
<tr>
<td>600°C</td>
<td>1</td>
<td>Eutectoid $\alpha + \gamma$ corresponding to 730°C. curve</td>
</tr>
<tr>
<td>590°C</td>
<td>1</td>
<td>Eutectoid $\alpha + \gamma$ corresponding to 730°C. curve</td>
</tr>
<tr>
<td>570°C</td>
<td>1</td>
<td>Eutectoid $\alpha + \gamma$ corresponding to 730°C. curve</td>
</tr>
<tr>
<td>500°C</td>
<td>1</td>
<td>Eutectoid $\alpha + \gamma$ corresponding to 730°C. curve</td>
</tr>
<tr>
<td>569°C + 4°C</td>
<td>18</td>
<td>Eutectoid $\alpha + \gamma$ corresponding to 730°C. curve</td>
</tr>
<tr>
<td>675°C 640°C</td>
<td>$1 + 6$</td>
<td>Eutectoid $\alpha + \gamma$ corresponding to 730°C. curve</td>
</tr>
</tbody>
</table>
Figs. 3.40 and 3.41, result while Figs. 3.42 - 3.47 show how the structure varies after various times at a constant soaking temperature.

(v) The effect of hot working in the $\alpha/\gamma$ region on the transformation product.

The results of section (iv) indicated that the low temperature structure appeared to be inherent in the material as received, but once destroyed could not be reproduced by any heat-treatment; the implication being that the manufacturing process had modified the structure. In order to simulate these conditions in the laboratory, specimens, following the high temperature anneal, were hot pressed to between 20% and 70% of their original thickness at approximately 650°C. This was performed in a modified mounting press with high frequency heating.

The pressed specimens were then re-cycled through the low temperature treatment and the typical low temperature structure was consistently produced (Fig.3.40). These specimens were then re-cycled through the basic heat treatments giving the same results as before.

A detailed analysis of the effect of varying percentages of deformation was not considered profitable due to the qualitative method of observing the worked and annealed structures.
The effect of time at temperature on the transformation product.

26% tin alloy isothermally transformed at 400°C.

800
750
700
650

Temperature ºC.

Log Time (secs.)
Fig. 3.40

100 1000 10,000 100,000

27% tin alloy isothermally transformed at 495°C

800
750
700
650

Temperature ºC.

Log Time (secs.)
Fig. 3.41

- Structure as low temperature curve Figs. 3.43 and 3.46.
- Intermediate Structure Figs. 3.44 and 3.47.
- Structure as high temperature curve Figs. 3.45 and 3.48.
The effect of increasing times at 756°C on the transformation product of the 26% tin alloy at 400°C.
The effect of increasing times at 730°C and subsequent hot working on the transformation product of the 27% tin alloy at 495°C.
SECTION III. The X-ray Diffraction Results

A. The results obtained on quenched alloys

The X-ray patterns obtained on quenched specimens were quite complicated consisting of a typical B.C.C. pattern with many extra lines. The lines obtained were rather spotty due to the large grain size but measurement was not a great problem. The high angle doublets were resolvable down to a Bragg angle of 47° for the main lattice lines of the photographs taken with the 114 m.m. camera (Fig.3.49).

Table 3.3 contains typical \(d\) values, corrected to three significant figures, which were obtained on the 25\%, 26\% and 27\% tin alloys in the as quenched condition. The stronger lines, typical of the simple B.C.C. pattern, are underlined and estimated optical intensities of the extra lines are included. The patterns obtained were independent of the quenching temperatures used and there was not any detectable difference when annealing treatments, similar to those necessary to cause changes in the isothermal transformation products, were used.

Experiments were also performed in order to eliminate possible experimental or metallurgical causes for the lines obtained. It was considered that any of the following phenomena may have resulted in the patterns obtained:

i Surface oxidation during heat treatment and quenching.

ii Decomposition to eutectoid during quenching.

iii Precipitation during holding at room temperature.
Fig. 3. 49. Typical X-ray diffraction patterns obtained from these alloys.

(Most of the faint superlattice lines are not reproduced.)
<table>
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</table>

* Not visible on all films  
vw Very Weak  
mw Moderately weak  
jd Just discernible.

w Weak
iv. Transformation to a martensitic structure during quenching.

i. Surface oxidation during heat treatment and quenching

Any oxide on the surface of the heat treated specimens was removed by very gentle polishing with Bluebell. As this produced no change in the X-ray pattern obtained, the possibility of surface oxidation was discounted.

ii. Decomposition to eutectoid during quenching

Microscopical examination of the X-ray specimens showed that they were typical of retained \( \beta + \gamma \).

iii. Precipitation during holding at room temperature

Precipitation at room temperature was considered as a possibility in view of the observed increase in the room temperature resistivity on ageing. However, there was no difference in the diffraction pattern whether the X-ray was taken immediately on quenching (and completed within 4 hours) or after the increase in resistance had occurred.

iv. Transformation to a martensitic structure during quenching.

The structure obviously does not consist largely of martensite otherwise this would have been evident on microscopic examination but this does not rule out the possibility of a small percentage of martensite. As Kurdjumow\(^{17}\) has stated that martensite forms in these alloys at sub-zero temperatures specimens were soaked in liquid air for one hour and then X-rayed. Other specimens were given light surface deformation by polishing with emery paper as
alternative means of inducing martensite formation. Typical results obtained for these alloys are shown in Table 3.4. The X-ray pattern of the 23% alloy, which is martensitic at room temperature when observed microscopically, is also included for comparison as are the 'd' values obtained for $\beta$ by Isaichev in alloys containing from 25 to 26.5% tin and reported in the A.S.T.M. index. High temperature annealing of the 25% tin alloy also results in more martensite formation (Column 4, Table 3.4.).

Generally, liquid air treatment or surface deformation caused only a slight change in the as quenched structure unless it was performed before the structure aged when a large percentage of martensite was formed (Column 3, Fig. 3.4.)

However, as a result of the treatment many lines present in the as quenched structure disappeared or decreased in intensity while a few became stronger indicating that they are caused by the martensite formation, while others are common to both structures. Thus while the formation of martensite could account for some of the lines present, many others are not accountable by this structure.

II. The results obtained at high temperature.

A limited number of diffraction experiments were carried out on the annealed filings of the 26.5% tin alloy at high temperature.

Exposures of up to 20 hours were required and the films obtained contained fairly broad lines, although the doublets were resolvable.

The 'd' spacings of these films are shown in Table 3.5, and it
Table 3.4.

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* Numbering corresponds to that used on Table 3.3

— Many faint lines present in these regions.
TABLE 3.4. (Continued)

\( \beta \) specics obtained on alloys treated to form martensite

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- **vs**: Very strong
- **ms**: Moderately strong
- **s**: Strong
- **w**: Weak
- **vw**: Very weak
- **m**: Medium
- **jm**: Just discernible

Intensity:
- **vs**: Very strong
- **ms**: Moderately strong
- **s**: Strong
- **w**: Weak
- **vw**: Very weak
- **m**: Medium
- **jm**: Just discernible
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* Not visible on all film.

** Numbering corresponds to that used on Table 3.3.
can be seen that only the film taken at 570°C. has any lines extra to those expected for the B.C.C. structure.

C. The results obtained on transformed specimens

To further the investigation into the nature of the isothermal transformation product below 400°C., a wire of the 27% tin alloy was isothermally transformed for one minute at 360°C., polished very gently to remove any oxide layer or lead coating, and then X-rayed. The (x + δ) structure of the same alloy was also X-rayed for comparison. The 'd' value obtained from these films are recorded in Table 3.6. although the values at higher Bragg angles were not measured because the patterns were very complex and the lines faint.
| 'd' spacings obtained from the 27% tin alloy air cooled and isothermally transformed. |
|------------------------|------------------------|

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**Intensities:**
- **vs** Very strong
- **s** Strong
- **ms** Moderately strong
- **vw** Very weak
- **w** Weak
- **mw** Moderately weak
- **jd** Just discernible
CHAPTER IV

THE EXPERIMENTAL RESULTS II

THE TERNARY COPPER-TIN-MICHEL ALLOYS

SECTION I Metallurgical examination of the heat treated alloys.

A. The determination of the equilibrium phases

The literature search indicated that a two phase ($\beta + \gamma$) region occurred in the ternary alloys; effort was therefore directed to substantiate this and to determine the extent of these regions.

Samples were annealed for five hours at 750°C. and air cooled, specimens from these were reheated to various temperatures in the $\beta$ and $\gamma$ regions for one hour, quenched and the structures examined microscopically. The results obtained are reported in Figs. 4.1 and 4.2, as partial vertical sections of the ternary phase diagram at 1 and 2 atomic per cent nickel respectively. Results from the resistivity experiments were also used to establish the temperatures of the phase boundaries more accurately. Figs. 4.3, 4.4 and 4.5 show these results plotted as part plans at 750°C, 700°C and 650°C respectively with the likely phase fields indicated.

Microscopically the two phases, $\beta$ and $\gamma$, are very similar being distinguishable only by a slight colour difference and having faint boundaries. Taken by themselves there is no microscopic distinction between $\beta$ and $\gamma$, and the homogenous structures were only labelled as $\beta$ or $\gamma$ by deduction. In two phase alloys the difference was clear; Fig. 4.6 shows areas of $\beta$ in a matrix.
Fig. 4.1. The copper tin phase diagram with 1 atomic per cent nickel
Fig. 4.2. The copper tin phase diagram with 2 atomic per cent nickel.
Fig. 4.5.
650°C.

Fig. 4.4.
700°C.

Fig. 4.3.
750°C.

Tentative isoplans of the copper tin nickel phase diagram at the temperatures indicated.
0.3% Nickel alloy - heated to 700°C and quenched.

**Structure** β in a matrix of γ

0.6% Nickel alloy - heated to 750°C then cooled to 700°C and quenched.

**Structure** networks and laths of γ surrounding and within β grains

27% tin binary alloy quenched from 750°C. - (β + γ) field Fig.1.1.
of γ and Fig. 4.7. shows networks and laths of γ surrounding and within the β grain. There is no difference between the hardness of the two phases in any one alloy.

These results indicate:

i. That there is a two phase region in these ternary alloys close to the (β + γ) field of Fig. 1.1.

ii. That increasing nickel content raises the temperature of the '586°C. arrest' and broadens the (β + γ) field.

B. The isothermal transformation experiments.

With the confirmation of the two phase structure in the above work, further experiments were initiated to associate this two phase region with reactions occurring in the binary alloys, and then, if possible, to use the association to clarify the nature of the reaction occurring in the binary system. It was considered that both these objectives could best be achieved with a set of experiments similar to those performed on the binary alloy. It was therefore decided to undertake isothermal transformation experiments on the 26.5% tin 0.8% nickel alloy after soaking in the β and the γ region, as this was the only alloy which exhibited 100% β and 100% γ at the appropriate different temperatures.

i. The isothermal transformation characteristics of the 26.5% tin 0.8% nickel alloy.

Isothermal transformation experiments were performed on this alloy in a similar manner to that used for the binary alloys, that
is specimens were annealed in the \( \gamma \) or \( \beta \) regions at 625°C. or 750°C respectively and then transformed in the \((\alpha+\delta)\) region.

The isothermal transformation curves are shown in Figs. 4.9 and 4.10. Compared with the isothermal transformation curves of the binary alloys, these curves are very similar at isothermal temperatures above 450°C. At approximately 450°C, an additional phase appears in these alloys which has a similar morphology to the \( \beta^* \) phase occurring at approximately 400°C in the binary alloys. A change in the slope of the 'finish' curves also occurs. The \( \beta^* \) phase occurs more readily in these alloys and therefore is more easily detectable so that a dotted line is included on these diagrams to indicate the start of its formation.

ii. The morphology of the 26.5% tin 0.8% nickel alloy.

a. After annealing at 625°C.

The eutectoid structure in this alloy at high sub-eutectoid temperatures is formed in a similar manner to that of the binary alloys. Fig. 4.11, transformed at 512°C, shows a fine \((\alpha+\delta)\) eutectoid structure which is typical of the structure formed in the binary alloys. The transformation of this alloy proceeds in a similar manner to below 480°C, but the structure becomes finer.

At lower temperatures the reaction occurs at the grain boundaries and at approximately 460°C. \( \beta^* \) starts to form as fine needles towards the end of the transformation (Fig. 4.12). As the temperature is decreased further \( \beta^* \) forms as the primary phase at many nuclei and is followed by some \((\alpha+\delta)\) eutectoid
Fig. 4.9. 0.8% Nickel alloy Time-Temperature Transformation Curve. Specimens annealed for 120 mins. at 750°C.
Fig. 4. 0.0% Nickel alloy Time-Temperature Transformation Curve. Specimens annealed for 120 mins. at 625°C.
0.8% Nickel alloy annealed at 625°C and transformed for 120 secs. at 512°C.

Structure - A fine (α+γ) eutectoid

0.8% Nickel alloy annealed at 625°C and transformed for 30 secs. at 460°C.

Structure (α+γ) eutectoid forming from the prior β grain boundaries with β* starting to form within the grains.
forming at the prior $\beta$ boundaries (Fig. 4.13).

b. After annealing at 750°C.

At high sub-eutectoid temperatures the eutectoid reaction again takes the characteristic form as Fig. 4.14, transformed at 520°C. shows a coarse eutectoid structure containing some primary $\alpha$. The structure is coarser than the comparable low temperature structure because of the higher transformation temperature and because of the grain size effect resulting from the higher annealing temperatures. As primary $\alpha$ formation ceases with decreasing temperature, the reaction takes a Widmannstätten eutectoid form growing both from the grain boundaries and within the grains (Fig. 4.15). At lower temperatures the number of intergranular nucleation sites decreases and intergranular eutectoid formation decreases as shown in Fig. 4.16, transformed at 448°C. Only at temperatures below this does $\beta^\ast$ occur in its characteristic form as shown in Fig. 4.17.

iii The effect of soaking temperature on the transformation product.

Comparison of the above transformation curves indicates that the effect of annealing temperature on this nickel containing alloy is similar to that obtained for the binary alloys at high isothermal temperatures. High temperature annealing again favours the formation of $\alpha$ which nucleates as a primary phase to lower isothermal temperatures than after the low temperature annealing. If the analogy were to continue to lower temperature one would expect the eutectoid structure to be formed over the remainder of the
Fig. 4.13  
0.3\% nickel alloy annealed at 625°C and transformed for 5 secs. at 420°C.

Structure  Needles of primary \( \beta^* \) nuclei with \((\alpha+\delta)\) eutectoid forming from the prior \( \beta \) boundaries - see below.

Fig. 4.13a  
27\% tin alloy annealed at 750°C and transformed for 5 secs. at 397°C.

Structure  Needles of primary \( \beta^* \) with \((\alpha+\delta)\) eutectoid forming at the prior \( \beta \) boundaries and as degenerate cuboids (dark) within the grains.
Fig. 4.14  x 210
0.8% Nickel alloy annealed at 750°C and transformed for 300 secs. at 522°C.
Structure  Primary α (light) with a coarse (α+γ) eutectoid forming in a matrix of β.

Fig. 4.15  x 210
0.8% Nickel alloy annealed at 750°C and transformed for 10 secs. at 470°C.
Structure  Widmannstätten eutectoid of (α+γ) forming from the prior β grain boundaries and within the grains of β.
Fig. 4.16. x 135
0.8% Nickel alloy annealed at 750°C and transformed
for 20 secs. at 440°C.
Structure Grain boundary eutectoid of (α+γ) with some intergranular
lenticular shaped areas of eutectoid forming.

Fig. 4.17 x 620
0.8% Nickel alloy annealed at 750°C and transformed
for 5 secs. at 422°C.
Structure (α+γ) eutectoid forming from the prior β grain boundaries
with some needles of β within the grains.
temperature range following the high temperature soaking treatment and a range of eutectoid formation followed by the formation of primary $\gamma$ for the low temperature annealing. The expected structure is realised for the high temperature soaking treatment but it is suggested that the strong tendency to form $\beta^*$ following the low temperature annealing results in this becoming the primary phase below 450°C, and so masking any formation of primary $\gamma$.

Thus in this alloy it is seen that the low temperature anneal favours the formation of $\beta^*$. A similar effect was not observed in the binary alloys although it would have been smaller and therefore less easily detected because of the less pronounced formation of $\beta^*$.

iv. The isothermal transformation of $\beta$ to $\gamma$.

To study the nature of the $\beta$ to $\gamma$ transformation specimens were annealed at 750°C in the $\beta$ region and isothermally transformed at temperature around the $(\beta + \gamma)$ field at 700°C.

However, the isothermal transformation apparatus was not designed to operate with the lead bath at so high a temperature, while lead at 700°C would rapidly dissolve any specimens immersed in it. The lead was therefore replaced by a hygroscopic salt bath consisting of a mixture of calcium, barium and sodium chlorides and by operating the furnace at maximum power, the required temperatures were obtained.

Accurate transformation curves could not be obtained because of the slower cooling rates resulting from the small differential
quench and the lower conductivity salt baths. As a result it was not possible to prevent $\rho$ from transforming to $\gamma$ during the cooling. It was however, possible to observe the general growth mechanism of the second phase in the two phase region.

During transformation the $\gamma$ formed initially as a fine grain boundary and uniform Widmannstatten precipitate (Fig.4.18). It was estimated that precipitation was complete after two seconds at 700°C. On holding at 700°C, the precipitate rapidly grew into a globular form (Figs.4.19 and 4.20).

When the alloy was transformed at temperatures just below the ($\rho$+$/gamma$) region $\rho$ rapidly transformed to $\gamma$ while at slightly lower temperatures the reaction was not observed and it was therefore assumed that it had gone to completion during the cooling operation.
The precipitation of $\gamma$ in a matrix of $\beta$ during isothermal transformation of the 0.8% nickel alloy at 690°C after annealing at 750°C.
SECTION II. The electrical resistivity results

A. Measurements obtained at elevated temperatures.

Resistance temperature curves were taken on the alloy containing 26.5\% tin, 0.3\% nickel and 25.5\% tin, 1.6\% nickel in a similar manner to that used for the binary alloys and the results are shown in Figs. 4.21 and 4.22, respectively.

(i) The resistance change associated with the eutectoid reaction $\alpha + \beta \rightarrow \gamma$

Examination of these curves immediately shows one major difference from the binary alloys; there is an increase in resistance during the eutectoid transformation on heating of approximately 4 micro-ohms per cm$^3$ for both these alloys compared with a decrease of approximately 6.5 micro-ohms per cm$^3$ for the binary 26\% tin alloy.

The temperature of the eutectoid reaction is raised by approximately 10°C. with the addition of 2 atomic per cent nickel.

(ii) The resistance change due to the solution of primary $\alpha$.

Despite the anomaly described above, the solution of $\alpha$ in $\beta$ or $\gamma$ results in a small increase in resistance in a similar manner to that observed in the binary alloys. However, on heating the as prepared specimens (Ref. Chapter II) the solution temperatures are 605°C. and 655°C. respectively for the 1 and 2 atomic per cent nickel alloy but these temperatures are raised to 620°C. and 670°C. respectively by annealing in the region.
Fig. 4.21 0.3% Nickel Resistivity Temperature Curve

<table>
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<tr>
<th>Specimen</th>
<th>Heating Rate °C./min.</th>
<th>Time at Temp.</th>
<th>Cooling Rate °C./min.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
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<td>360 mins.</td>
<td>□ 2.8</td>
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<tr>
<td>▲ 1.3</td>
<td></td>
<td>120 mins.</td>
<td>□ 1.3</td>
</tr>
<tr>
<td>2</td>
<td>x 2.5</td>
<td>120 mins.</td>
<td>□ 2.1</td>
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</tbody>
</table>

Melting point: 153.8°C.
Resistivity Curves 1.0% Nickel Alloy - Fig. 4.2

Heat Treatment Cycle

<table>
<thead>
<tr>
<th>Specimen</th>
<th>Heating Rate</th>
<th>Time at Temperature</th>
<th>Cooling Rate</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>6.5°C/min</td>
<td>40 mins @ 700°C</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>3.5°C/min</td>
<td>70 mins @ 715°C</td>
<td>1.7°C/min (715-620°C)</td>
</tr>
<tr>
<td></td>
<td>reheated</td>
<td></td>
<td>2.0°C/min (670-500°C)</td>
</tr>
<tr>
<td></td>
<td>620-670°C</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>1.5°C/min</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
(iii) The apparent resistivity temperature curves in the $\beta + \gamma$ phase field.

The resistance temperature curves obtained by heating and cooling through the $\beta$, $(\beta + \gamma)$ and $\gamma$ regions are smooth without any irregularity. There is no indication whatsoever of the $\beta \rightarrow \gamma$ transformation and this applies irrespective of the prior treatment of the alloy.

(iv) The effect of holding at high temperature

On holding these alloys at high temperatures in the $\beta$ region there is a small decrease of 0.2 micro ohms per cm$^2$ in the resistivity of the 1.6% nickel alloy similar to the decrease observed in the 26% and 27% tin binary alloys.

However, there was no similar decrease observed in the 0.8% nickel alloy although it was held for 120 minutes at 720°C. This is not the result that would be expected from this alloy as in all other respects this alloy behaves similarly to the other alloys which do show a resistance on annealing in the region, and it appears that in this alloy the annealing reaction occurs without a resistance change.

In the attempt to discover a resistance change, the second 0.8% nickel alloy was allowed to become semi-molten and then cooled down. Under these conditions its resistance was higher on cooling but this is almost certainly due to some dimensional change resulting from liquid formation.
B. The resistivity of the quenched specimens

Low temperature resistivity experiments were performed on the 26.5% tin 0.3% nickel alloy in an identical manner to those performed on the binary alloys. The heat treatment applied to the above alloy was of the following different forms:

(i) The effect of increasing annealing temperature on the resistance of the as prepared sample.

(ii) Resistance temperature curves on annealed specimen by

(a) Heating directly to temperature, holding and quenching

(b) Heating to 750°C, holding, then furnace cooling to a lower temperature in the \( \beta + \gamma \) region, holding and then quenching.

Method (i) combined the effect of annealing and varying temperature, while method (ii) investigated the effect of temperature only, and at the same time indicating any possible effect resulting from approaching the soaking temperature from opposite directions.

The summary of the results obtained from these experiments are shown in Fig. 4.23. It is interesting to observe that with treatments (i) and (ii) (b) the resistivity is a minimum after annealing at 700°C, where the two phase \( \beta + \gamma \) structure exists, while after treatment (ii) (b) the resistivity is a maximum at this temperature.
Fig. 4.23. Low temperature resistivity-temperature curves of the 0.8% Ni alloy. Resistivity measured at 0°C.

1. The effect of increasing annealing temperature. - ref. text(i)
2. The effect of heating to 750°C, then cooling to the quenching temperature. - ref. text(II) b
3. The resistivity-temperature curve. - ref. text (II) a
SECTION III. The X-ray diffraction results.

A. The results obtained on quenched specimens

The X-ray results obtained on the ternary alloys containing 26.5\% tin 0.8\% nickel and 25.4\% tin 1.6\% nickel are shown in Table 4.1.

The results obtained from these alloys, which were obtained on the specimens quenched from the $\beta$ ($\beta + \gamma$) and $\gamma$ regions, indicate that there is no difference between the structure of $\beta$ or $\gamma$ after quenching. They also show that their structure is the same as the structure of quenched $\beta$ in the binary alloys.
### Table 4.1

<table>
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<tr>
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<th>0.8% Nickel alloy</th>
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<th>1.6% Nickel alloy</th>
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<td>Quenched from 750°C</td>
<td>Quenched from 670°C</td>
<td>Quenched from 750°C</td>
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<td>d'</td>
<td>Intensity</td>
<td>d'</td>
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<td>2.96 vw</td>
<td>2.96 vw</td>
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<td>0.994 v</td>
<td>0.995 v</td>
<td>0.995 v</td>
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<td>0.776</td>
<td>0.777</td>
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</table>

*Not visible on all films*

- **w**: Weak
- **vv**: Very weak
- **jd**: Just discernible.
CHAPTER V
THE INTERPRETATION OF THE X-RAY DIFFRACTION PATTERN

SECTION I  The structure of $\beta$ after quenching

The X-ray powder patterns obtained from the quenched alloys, both binary and ternary, whether hot worked or annealed, $\beta$, $(\beta + \gamma)$ or $\gamma$, were all of the same form giving similar lines and 'd' values. The patterns obtained at high temperatures also gave similar 'd' values although there were less lines present.

Experimental techniques have shown that some of the lines present on the quenched pattern result from the presence of some martensite but this cannot account for all of the extra lines present.

To facilitate indexing of these lines, the diffraction pattern expected from the alloys according to the results of Hendus and Knodler was calculated assuming the lattice parameter of the cell (Fig. 1.7) to be 6.0 Å.

The reflections expected are shown in Table 5.1 column 1 together with their approximate 'd' values (column 2). The expected relative intensity of these lines was also calculated from the D-03 cell suggested by Hendus & Knodler using the formula:
where $T = \text{calculated intensity}$

$$I \propto \left(1 + \frac{C_\theta^2 \cos^2 \theta}{\sin^2 \theta \cos \theta}\right) \rho A \beta F^2$$

The absorption and temperature factor were considered negligible compared with the remainder, values for which were obtained from standard works of reference after calculating $\theta$ for a lattice parameter of $6\AA$.

Column 3 Table 5.1. shows the relative intensities expected for stoichiometric order at 25 atomic per cent tin. However, these alloys only contain approximately 15 atomic per cent tin and so the intensities were re-calculated for this tin concentration (Column 4 Table 5.1.) assuming that the excess copper atoms, above the stoichiometric composition, replace tin atoms randomly within the ordered lattice.

It is, of course, possible that further ordering may take place on the superlattice sites only between the excess copper atoms and the tin atoms. Ordering of this type has been suggested.
TABLE 5.1.
Calculated 'd' spacings and intensities expected from Cu$_3$Sn
D-0$_3$ of superlattice cell and extra lines expected from
Cu$_3$Sn$_3$ cell (Fig. 2.50)

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<th>h.k.l. (F.C.C.)</th>
<th>'d'</th>
<th>Intensity</th>
<th>Intensity</th>
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<td>17250</td>
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<td>553 731</td>
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<td>368</td>
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Extra reflections from Cu$_3$Sn$_3$

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</thead>
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<td>274</td>
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<td>139</td>
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<td>310</td>
<td>69</td>
</tr>
<tr>
<td>321</td>
<td>73</td>
</tr>
</tbody>
</table>

Numbering corresponds to that used on Tables 3.3. and 4.1.
by Taylor and Jones for iron aluminium alloys at the composition

\[ \text{Fe}_{13}\text{Al}_3 \]  Cu_{13}\text{Sn}_3 occurs at approximately 30 weight per cent tin

and therefore similar ordering is possible in these alloys.

The tentative unit cell is shown in Fig. 5.1, and Column 5

(Table 5.1.) indicates the calculated reflections and

intensities expected from the low angle lines of such a structure.

As can be seen, many extra low angle lines of observable intensity

would result from this structure and as these do not occur it is

concluded that this type of ordering does not exist in these

copper tin alloys.

Comparison of the calculated 'd' spacings, Column 2 Table 5.1.

with those reported in Table 3.1, indicates good agreement with

but a few exceptions which are accounted for by the presence

of martensite. The intensities (Column 4 Table 5.1.) also are

in the right order of magnitude although some of the weaker

lines may be absent. An exception to this is the \( (200) \) line

which is generally much weaker than expected but as these X-rays

were performed on hot-roller material it is possible that some

texture present may have modified the intensity of this line,

although texture is obviously not serious in view of the general

agreement between the calculated and expected results.

Lattice parameters were calculated for these patterns on the

basis of the \( D-G \) structure and are shown in Table 5.2. The values
Superlattice cell
Disordered B.C.C.
Copper
Tin

Tentative Cu$_{73}$Sn$_{27}$ Unit Cell

Fig. 5.1.
were computed using seven figure sine tables and the final values were obtained by plotting $a(hkl) \times \sin\theta \left( \frac{C_0^2 \theta + \frac{L}{2} \theta^2}{1 + \frac{L}{2} \theta^2} \right)$ as suggested by Nelson and Riley and extrapolating to $\Theta = 90^\circ$.

A. The effect of high temperature annealing on the lattice parameter of quenched B.

Although annealing caused no detectable change in the powder pattern of these alloys, it was thought that the lattice parameter might be affected. Therefore, the 27.5% tin alloy was X-rayed in the as-received condition after quenching from 600°C, then annealed so as to cause the changes observed by the electrical resistivity and isothermal transformation experiments, and then re-quenched from 600°C and X-rayed again. Table 5.2 shows that there is a decrease in the lattice parameter after this treatment.

B. The accuracy of lattice parameter measurements.

The line corresponding to the 321 B.C.C. plane is considered to have been measured with the highest accuracy, for although the 731 F.C.C. super lattice line occurs at a higher Bragg angle, it was fainter and broader. The 321 line occurs at an angle of approximately 75° and could be measured to within 0.025°. When photographed in the 114 mm. camera this resulted in a difference of 0.0002 in the value of sine $\Theta$. Thus an accuracy of $\pm 0.01\%$ is expected from the results obtained with the large Phillips camera.
TABLE 5.2.
The lattice parameters of the quenched alloys

<table>
<thead>
<tr>
<th>Quenching temperature</th>
<th>Lattice Parameter</th>
<th>4</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>25% tin</td>
<td>26% tin</td>
</tr>
<tr>
<td>550°C</td>
<td>5.9545</td>
<td></td>
</tr>
<tr>
<td>600°C</td>
<td>5.9576</td>
<td>5.9714</td>
</tr>
<tr>
<td>650°C</td>
<td>5.9588</td>
<td>5.9720</td>
</tr>
<tr>
<td>670°C</td>
<td></td>
<td>5.9770</td>
</tr>
<tr>
<td>680°C</td>
<td></td>
<td></td>
</tr>
<tr>
<td>700°C</td>
<td>5.9597</td>
<td>5.9730</td>
</tr>
<tr>
<td>750°C</td>
<td>5.9610</td>
<td>5.97202</td>
</tr>
</tbody>
</table>

1. Lattice parameter of the β which co-existed at this quenching temperature = 3.705

2. 1 hour at 750°C

3. Two hours at 750°C furnace cooled to 600°C, held 1 hour then quenched.

4. All the lattice parameters quoted apply to the F.C.C. super lattice cell - parameters for the B.C.C. cell are half the values shown.
C. The structure of $\beta$ at high temperature.

The films obtained at high temperature were readily indexed on a simple B.C.C. cell with one exception - the film obtained at 570°C. This contained some extra lines which, however, agreed well with the formation of a Cu$_2$Sn type super lattice. The lattice parameters obtained are shown in Table 5.3.

D. The structure of the transformed specimens

To resolve the complex X-ray patterns obtained from the isothermally transformed specimens, resort was again made to the process of intuitively comparing 'd' spacings of likely structures. The 'd' spacings for the F.C.C. $\alpha$ are shown in Column 1 Table 5.4. and lines 10, 13, 23, 27, and 29 of the ($\alpha + \delta$) structure Table 3.6. agree well with the first five values. The remaining lines are assumed to be caused by the $\delta$ phase for which no 'd' spacings are available. However, it is worth noting that many of the remaining stronger lines, notably 10, 17, 25 and 30, correspond to 'd' spacings found for the $\beta$ structure.

The most notable observation from the pattern obtained from the specimen isothermally transformed at 360°C, is that the lines corresponding to the $\alpha$ phase, are present only faintly, while new lines, less intense and at a higher Bragg angle, have appeared. These new lines (11, 14 and 24) are still capable of being indexed on a F.C.C. pattern. They are shown in column 2, Table 5.4.
The lattice parameter of the 26% tin alloy at temperature

<table>
<thead>
<tr>
<th>X-ray Temperature</th>
<th>Lattice Parameter 1</th>
</tr>
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<tr>
<td>570°C</td>
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<tr>
<td>590°C</td>
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<tr>
<td>650°C</td>
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</tr>
<tr>
<td>700°C</td>
<td>6.041</td>
</tr>
<tr>
<td>750°C</td>
<td>6.047</td>
</tr>
</tbody>
</table>

1. All the lattice parameters quoted apply to the F.C.C. super-lattice cell. Parameters for the F.C.C. cell are half the values shown.
with their calculated lattice spacings which leads to an approximate lattice parameter of 3.6 Å for this phase. This corresponds to an \( \alpha \) phase of much lower tin content.

The main reflections of the \( \delta \) phase are still present but of lower intensity but many of the weaker lines have disappeared and are replaced by other faint lines. These lines were compared against those reported for the \( \epsilon \) phase in the A.S.T.I. index (shown Column 3, Table 5.4.). Close comparison between these 'd' values and those of the film show that there is a new line corresponding to 'd' = 2.38; while 2.16 and 2.08 are masked by the broad line occurring at this value and that there are other lines which correspond down to 'd' = 1.15 without certainly distinguishing the structure.

Reference to the phase diagram (Fig.1.1.) shows that a low tin \( \alpha \) phase is to be expected with the \( \epsilon \) phase and therefore it is proposed that the extra lines are caused by the presence of some \( \alpha + \epsilon \) eutectoid which is therefore, the additional structure in the isothermal transformation product below 400°C.
The interpretation of the structure obtained during air cooling and isothermal transformation of the 27.5% tin alloy — see text.

<table>
<thead>
<tr>
<th>(h.k.l)</th>
<th>1 'd' spacings for F.C.C.</th>
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<tbody>
<tr>
<td></td>
<td>a = 3.70</td>
</tr>
<tr>
<td>10</td>
<td>3</td>
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<td>13</td>
<td>4</td>
</tr>
<tr>
<td>23</td>
<td>8</td>
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<td>27</td>
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<td>29</td>
<td>12</td>
</tr>
<tr>
<td>16</td>
<td>0.925</td>
</tr>
<tr>
<td>19</td>
<td>0.850</td>
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<tr>
<td>20</td>
<td>0.828</td>
</tr>
<tr>
<td>24</td>
<td>0.755</td>
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</tbody>
</table>

<p>| 2 lattice parameters from 'd' spacings on Table 3.6. |</p>
<table>
<thead>
<tr>
<th>d</th>
<th>a</th>
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<tbody>
<tr>
<td>2.38</td>
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<tr>
<td>2.16</td>
<td>40</td>
</tr>
<tr>
<td>2.08</td>
<td>100</td>
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<tr>
<td>1.60</td>
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<td>0.85</td>
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<tr>
<td>0.83</td>
<td>12</td>
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</table>

<p>| Cu S. Jones &amp; Evans |</p>
<table>
<thead>
<tr>
<th>d</th>
<th>1/I_1</th>
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<tbody>
<tr>
<td>2.38</td>
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<td>2.16</td>
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<td>0.85</td>
<td>24</td>
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<tr>
<td>0.83</td>
<td>12</td>
</tr>
</tbody>
</table>

* Numbering corresponds to that used on Table 3.6. only
CHAPTER VI
DISCUSSION

SECTION 1 The Isothermal decomposition of the $\beta$ and $\gamma$ bronzes

Before discussing the specific effect of annealing treatment on the decomposition of these alloys, it is useful to make a brief qualitative examination of the eutectoid reaction occurring in these alloys.

When compared with '3' curves obtained by previous workers, the results obtained here agree well with those of Miodownik (Fig. 1.13) and Nagasaki (Fig. 1.9) but only poorly with the results of Hosoi (Fig. 1.10) whose alloys appeared to transform much more slowly and without any primary phase formation.

The transformation curves indicate that the suppression of precipitation is readily achieved while $\delta$ precipitation is very difficult to prevent. This is analogous to the precipitation of $\alpha$ and $\gamma$ from $\beta$ brass. The $\delta$ forms with the same rosette structure as $\gamma$ brass and the kinetics of reaction are probably due to the crystallographic similarity between $\delta$ and $\beta$ or $\gamma$ as suggested by Hassalski for the brasses. This has the effect shown in Fig. 6.1: so that at sub-eutectoid temperatures the metastable eutectoid is shifted towards lower tin contents as exemplified by the 27% tin alloy which precipitates primary $\alpha$ at high transformation temperatures and primary $\delta$ at lower temperatures.

The decomposition sequences of these alloys change from intergranular to grain boundary and back to intergranular over
Fig. 6.1. The effect of the transformation temperature on the eutectoid composition.

The 'finish' of primary $\alpha$ formation in 'S' curves obtained after high temperature annealing.

The 'start' of primary $\delta$ formation in 'S' curves obtained after high temperature annealing.
quite small changes in transformation temperature but of particular interest are the cuboids of eutectoid formed, generally in the lower tin alloys tested. A similar structure has been observed on decomposition of the $\beta$ phase in copper aluminium alloys. High magnification indicates that these cuboids are $\gamma$ nucleated and it seems probably that under certain conditions the rosettes of $\gamma$ grow in particular directions in the $\beta$ and then the $\alpha$ forms between the rosette arms.

At temperatures below $400^\circ{C}$, another phase becomes evident in the microstructure and X-ray work has indicated it to be $\epsilon$. Thus it appears that the temperature of the $\gamma \rightarrow \alpha + \epsilon$ eutectoid may be higher than previously reported. It also indicates that while the reaction $\gamma \rightarrow \alpha + \epsilon$ takes several thousands of hours to complete at $350^\circ{C}$, $\alpha + \epsilon$ will form quite readily from $\beta$ if the $(\alpha + \delta)$ reaction is suppressed. Initially, the $(\alpha + \epsilon)$ forms with $(\alpha + \delta)$ but it is to be expected that $(\alpha + \epsilon)$ would form alone if lower transformation temperatures were used.

It seems highly probable that the large electrical resistance decrease observed on reheating quenched $\beta$ alloys (see Fig.1.12) is associated with the formation of $(\alpha + \epsilon)$.

**The effect of Nickel on the decomposition of the $\alpha/\gamma$ bronzes**

Nickel raises the temperature of the $(\alpha + \delta)$ eutectoid but otherwise has little effect on the transformation morphology of the $(\alpha + \delta)$ eutectoid.
Nickel also raises the temperature at which the $\varepsilon$ is first observed in the structure and this indicates that the ternary diagrams of Veselka\textsuperscript{27} and Eash and Upthegrove\textsuperscript{36} may be in need of extensive revision as they were unaware of the existence of this phase. Examination of the photomicrographs produced by Eash and Upthegrove shows that the structure designated $\Theta$ by these workers has the same morphology as the $\varepsilon$ phase formed in these alloys.
SECTION II  The \( \beta / \gamma \) transformation

During the various experiments carried out it has been shown that annealing in the \( \beta \) and \( \gamma \) regions can cause changes in some of the physical properties and transformation characteristics of some of the alloys. It is pertinent to enquire whether the changes observed are related to the \( \beta / \gamma \) transformation under discussion, or whether they are related to some other change, or whether they are merely spurious effects possibly created by the experimental techniques used. It is also important to consider whether the nickel in the ternary alloys acts as a label for the \( \beta + \gamma \) field observed or whether the two phase region is a direct result of the nickel additions. In discussing the results obtained, all these alternatives will be considered but it is hoped that the reaction observed will be justified as occurring as a result of the \( \beta / \gamma \) transformation.

A. The effect of annealing on the transformation characteristics of binary copper tin alloys.

The results have shown that the isothermal decomposition products of these alloys depend upon several factors, notably:

(i) The composition of the alloy

(ii) The time and temperature of annealing.

(iii) The history of the alloy

(1) The composition of the alloy

The decomposition of alloys of highest and lowest tin content, 25\% and 28\% respectively, is unaffected by variations in the prior
treatment while the structure obtained in the alloys of intermediate tin content on isothermal decomposition at any particular temperature depends on factors (ii) and (iii) listed above.

(ii) The time and temperature of annealing

Annealing the 26 and 27\% tin alloys at a low temperature within the $\gamma$ region prior to isothermal decomposition results in a product which contains less $\alpha$ and more $\beta$ than when the identical alloy is annealed at high temperatures in the $\beta$ or $\gamma$ region. There is no demarcation 'high' and 'low' temperatures, a long time at a 'low' temperature being the equivalent to a short time at a 'high' temperature but in general terms high and low are used to denote the temperature and times used in the initial 'S' curve determination for each alloy examined.

(iii) The history of the alloy

It was further established that once the high temperature annealing had been completed it was impossible by further heat treatment, to obtain the isothermal decomposition product characteristic of the low temperature anneals. The low temperature structure could however, be reformed by hot working the alloy in the $\gamma$ region when the transformation product again depended on the annealing time and temperature.

Consideration of these results leads to the following possible explanations for the results obtained:

(a) Alloy segregation

(b) Embryo nucleation
(c) Favourable nucleation due to crystallographic symmetry

(d) Modification of the eutectoid composition due to the $\rho / \chi$ change.

(a) **Alloy segregation**

Although alloy homogenisation could account for many of the changes observed in these alloys it can be ruled out as a general explanation because individual specimens have been shown to form both types of isothermal transformation product on repeated treatment.

(b) **Embryonic nucleation**

It has been suggested that at temperatures just inside any phase field there are nuclei of the decomposing phase present. To account for the results obtained in these alloys it would imply that at low temperatures just inside the $\chi$ phase field nuclei of $\chi$ are present (as $\chi$ is the predominant phase after the low temperature treatment) for considerable times although the structure appears single phase microscopically. If this occurred it could account for the favoured nucleation of the $\chi$ phase after low temperature annealing of the 26% and 27% tin alloys. Effects of this type would be expected to occur on every heating following decomposition to a $\chi$ containing structure and also on the other alloys tested particularly the hypereutectoid alloy.

(e) **Favourable nucleation due to crystallographic symmetry**

If it is assumed that the changes observed are related to the
ordering observed by Hendus and Knodler\textsuperscript{19} and confirmed in the present work, then it might be expected that the low temperature structure is ordered and the high temperature structure disordered. The structures of $\beta$, $\delta$ and $\sigma$ are all basically body centred cubic with lattice parameters in the ratio $1:2:6$ and as $\sigma$ has tin atoms in ordered positions one would expect ordering to favour the formation of $\sigma$. From such a hypothesis one would expect the ordered 'low' temperature structure to decompose to a $\sigma$ rich eutectoid as is observed. But it has been shown that the low temperature structure is a non-equilibrium structure which is destroyed by annealing and only reformed by hot-working. It is hard to visualise how a structure can be brought to non-equilibrium order by hot-working.

(d) Modification of the eutectoid composition due to the \(\beta/\delta\) change.

However, it has been shown\textsuperscript{52} that deformation can destroy ordering, and more recently, this has been shown to be caused by the creation and passage of dislocations which results in the formation of anti-phase boundaries\textsuperscript{53}. If the hot-working has a similar disordering effect on the alloys containing 26, 27 and 28 tin then this implies that the structure obtained by hot-working and annealing at the low temperatures is disordered while high temperatures annealing forms equilibrium structure which is ordered. If it is further assumed that the $\beta/\delta$ transformation
of Fig. 1.1. is associated with this ordering then $\beta_{LT}$ corresponds to $\beta$ established by hot working and $\beta_{HT}$ corresponds to the equilibrium structure ($\gamma$ in Fig. 1.1.).

The results expected from these hypothesis can be compared with those obtained experimentally by reference to Fig. 6.2, which is part of the copper-tin phase diagram but containing only those lines which have been experimentally determined. To these have been added a metastable $\beta \rightarrow \alpha + \delta$ eutectoid which was obtained by 'suppressing' the kink in the $(\alpha + \beta)/\beta$ phase boundary caused by the 586°C arrest and drawing the $\beta/(\alpha + \beta)$ and the $\beta/(\beta + \delta)$ boundaries parallel to the $\gamma/(\alpha + \delta)$ and the $\gamma/(\gamma + \delta)$ boundaries respectively. The eutectoid temperature is unchanged as $\beta_{LT}$ and $\beta_{HT}$ have been shown to form a $\alpha + \delta$ structure at 520°C.

Considering these alloys $\beta_{LT}$ would then be expected to decompose by the metastable $\beta \rightarrow \alpha + \delta$ eutectoid which, because it is at a lower tin content, results in less supersaturation of $\alpha$ than the $\gamma \rightarrow \alpha + \delta$ eutectoid and a greater supersaturation of $\delta$. Thus the eutectoid structure resulting from $\beta_{LT}$ would be expected to contain less $\alpha$ and more $\delta$ than the eutectoid structure resulting from $\beta_{HT}$. Additionally, $\delta$ would be expected to form at a higher temperature as the $\beta/(\beta + \delta)$ boundary lies above the $\gamma/(\gamma + \delta)$ boundary. This is, in fact, what is observed in the 26% and 27% tin alloys.
The effect of hot working on the eutectoid composition - see text.

After high temperature annealing, alloys decomposed by $\gamma \rightarrow \alpha + \delta$ eutectoid giving 'S' curves (Figs. 3.15 and 3.17).

After low temperature annealing, alloys decomposed by $\beta \rightarrow \alpha + \delta$ eutectoid giving 'S' curves Figs. 3.14 and 3.18.
These reactions do not apply to the 25\% tin alloy because this alloy is of lower tin content and it is suggested, is not ordered at temperature and so cannot be disordered by hot-working.

As the tin content increases the ordering energy increases rapidly, thus the 26\% tin alloy is ordered, but is readily disordered by hot working and requires long annealing times to reorder. In the 27\% tin alloy, the driving force for order is higher and shorter annealing times are required while in the 28\% tin alloy the ordering energy is high so that hot working, which is very difficult to perform, does not destroy ordering and only one type of transformation product is observed.

The hypothesis, therefore, explains all the observations with reasonable success.

E. The effect of annealing on the transformation characteristics of the 26\% tin 0.8\% nickel alloy.

The effect of one atomic per cent or more nickel on the binary copper tin phase diagram has been shown to be the formation of a microscopic two phase $(\beta+\gamma)$ field. This fact makes deductions based on these systems simpler as they can be related directly to the equilibrium phase, $\beta$ or $\gamma$ which is present at the temperature concerned.

The eutectoid structure obtained on annealing the 26\% tin 0.8\% nickel alloy has been shown to depend on the annealing temperature in a similar way to the binary alloys. Examination of the transformation products, bearing in mind the increased
tendency to form the $\varepsilon$ phase, shows an increased tendency to form $\alpha$ after high temperature annealing which is in accord with the results from the binary alloys. Thus a completely analogous explanation applies as reference to Fig.6.3 will indicate.

A further point is however evident: the $\beta \rightarrow \alpha + \gamma$ eutectoid structure results from annealing in the $\delta$ region but the alloy is not under equilibrium because of the hot working and short annealing time. However the $\gamma \rightarrow \alpha + \gamma$ structure results after annealing in the $\delta$ region where the alloy is under equilibrium, thus the alloy must transform from $\beta$ to $\gamma$ on cooling prior to eutectoid transformation. Further evidence for this was obtained by the direct experiments attempted on the $\beta \rightarrow \gamma$ transformation in this alloy. This implies, that once the hot working effect has been destroyed, the cooling rates used are too slow to prevent any $\beta \rightarrow \gamma$ transformation occurring and therefore the annealing temperatures do not define the equilibrium place present.

That the ($\beta + \gamma$) two phase regions are retained on quenching does not destroy this argument because alloys held in this region segregate into $\beta$ and $\gamma$ of different composition as disclosed by micro probe analysis whereas during fast cooling $\beta$ can transform to $\gamma$ of the same composition without any long range diffusion.

C. The effect of annealing on the resistance temperature curves.

Any changes observed during the high temperature resistance measurement of these alloys are directly comparable with the
Fig. 6.3. The effect of hot working on the eutectoid composition of the ternary alloys.

- After high temperature annealing, alloys decompose by the $\delta \rightarrow \alpha + \delta$ eutectoid giving 'S' curve Fig. 4.9.
- After low temperature annealing, alloys decompose by the $\beta \rightarrow \alpha + \delta$ eutectoid giving 'S' curve Fig. 4.10.
reactions occurring during annealing of the alloys prior to isothermal transformation except that the heating and cooling rates used were slower.

(i) The $\alpha$ solution temperature

The initial heating curve for the 26.5\% tin 0.8\% nickel alloys shows that the $\alpha$ solution temperature is 605\°C, whereas on reheating after annealing and cooling the $\alpha$ solution temperature is 620\°C. Comparison with Fig. 6.3 shows that 605\°C agrees well with the temperature of the $\beta/($ $\alpha + \beta$ ) boundary and 620\°C with the $\gamma/($ $\alpha + \gamma$ ) boundary. Similar changes are observed with the 1.6\% nickel alloy.

These observations present excellent additional evidence for the hypothesis advanced on the effect of annealing and also directly relate the annealing with the $\beta$ to $\gamma$ transformation.

A similar effect was not clearly observed in the binary alloys but in the 26.5\% and 27.5\% tin alloys where it would be expected, the amount of primary $\alpha$ present was small, and, at the heating rates used, the eutectoid reaction was barely complete before all the primary $\alpha$ was in solution.

(ii) The resistance temperature curve

There were no discontinuities of any sort in the resistance temperature curves of any of these alloys. This also applies to the ternary alloys on heating through the $\beta + \gamma$ field which indicates that $\beta$ and $\gamma$ have a very similar resistance.
(iii) The effect of annealing on the resistivity.

When the binary alloys are held at a high temperature within the $\beta$ or $\gamma$ regions at times corresponding to those used prior to isothermal transformation, there is a small decrease in the resistance of the 26\% and 27\% tin alloys but no change in the resistance of the 25\% and 20\% tin alloys. This decrease is permanent and is not observed if the alloys are annealed prior to resistance measurements and therefore is associated with the $\beta$ to $\gamma$ change.

In the ternary alloys the 1.6\% nickel alloy shows a similar resistance decrease but the 0.8\% nickel alloy does not. In other respects (e.g. the effect of annealing on the transformation product, the change of $\alpha$ solution temperature) the 0.8\% nickel alloy behaves similarly to the other alloys which exhibit a resistance change during annealing. It is therefore suggested that no resistivity decrease is observed in this alloy, not because the annealing reaction does not occur, but because the resistivity change is smaller and outside the limits of detection.

From the results discussed so far, it has been shown that the annealing effects in the ternary alloys occur as a result of the $\beta \rightarrow \gamma$ transformation and, because the effects observed are so very similar, it is also concluded that the same reaction occurs in the binary alloys.
SECTION III  The Correlation of the results from metallographic, resistivity and X-ray experiments

From the results discussed so far the hypothesis is presented that the reactions observed in both the binary and ternary alloys are associated with the $\beta \rightarrow \gamma$ transformation and that this transformation involves the ordering of the $\beta$ phase. Further, the reactions are only observed at all because of the hot working which stabilises disorder at room temperature in alloys that normally order even during fast cooling.

However, there are two pieces of evidence which rule out this simple explanation: firstly there is a small decrease in the electrical resistance of the $\beta$ as annealing proceeds but no equivalent change on heating from the $\beta$ to the $\gamma$ field or vice versa; secondly all the alloys X-rayed at room temperature, except the 22% tin alloy show an ordered B.C.C. structure.

A. The resistivity result on annealing in the $\beta$ region.

To extend the hypothesis to account for these apparent anomalies it is first necessary to consider the effect of working on the structure of an ordered alloy. When a dislocation passes through an ordered lattice the two parts of the lattice on either side of the Burgers vector of the dislocation become out of phase with each other, thus one domain is split into two domains although each individually is still ordered. However, the passage of a second
dislocation on the same system makes the order in phase again except for the region separating the dislocations. Thus, in ordered systems, close to the stoichiometric composition dislocations have been shown to travel in pairs forming superdislocation to reduce the disordering effect. Little is known of dislocation structures well away from stoichiometric composition but it is probable that the equilibrium separation of the superdislocations is larger than at stoichiometry. Thus the effect of working is to decrease the domain size considerably without altering the order within each domain markedly, i.e. the long range order is decreased considerably but the short range order only slightly. In these alloys hot working is used so the alloys are recrystallising in situ with the dislocations annealing out but in the 26.2 and 27.2 tin alloys the driving force is not sufficient for the atom atom pairs to re-arrange themselves over the domains and so the atomic structure is predominantly that obtained by working. This does not apply to the 28.3 tin alloy which has a higher driving force and therefore orders during working.

It is the growth of the domains size with the removal of the domain walls which, it is suggested, results in the decrease in resistance on annealing but there is no subsequent change in resistance on long range disordering during heating from \( \gamma \) to \( \beta \). This is in agreement with the work of Sykes on CuAu where the growth of domain size was found to be the slow rate controlling
process of ordering; and also with the work of Newkirk et al.\textsuperscript{56} on cobalt-platinum where no electrical resistance decrease was observed on ordering with measurements made at temperature.

B. The low temperature X-ray results.

It has been indicated during the metallography of the ternary alloys that the $\beta \rightarrow \gamma$ equilibrium transformation is not suppressed by quenching, as occurs with other copper base phases e.g. copper aluminium\textsuperscript{57}, although the $\gamma \rightarrow \alpha + \delta$ reaction can be. This is borne out because the room temperature X-ray patterns of all the nickel containing alloys contain superlattice lines irrespective of specimen history.

In the binary alloys a $(\beta + \delta)$ field has not been found but if one is assumed to be in the same relative position as in the 0.8\% nickel alloy then a schematic diagram as shown in Fig. 6.4 will explain the observed results.

Line EC, extended into the $(\alpha + \delta)$ field to account for quenching effects, represents the $\beta \rightarrow \gamma$ change while the line shown is the martensite start temperature as determined by Kurdjumov\textsuperscript{17}. However, the present work disagrees with the results of Kurdjumow because alloys with 26.4 and 27.4 tin have been shown to contain a small proportion of martensite at room temperature. This indicates that the X-ray techniques of Kurdjumow were probably insensitive to small amounts of martensite especially so as he did not detect any ordering in these alloys which were
specifically stated to be disordered. They do, however, report a change in the structure of the martensite obtained at approximately this composition without detailing the actual change which is further indication of a change in the structure of the $\beta$. In view of these results it is probable that the true $M_s$ is actually some degrees above the reported value as shown $M_{s1}$.

Fig. 6.4 indicates that quenched alloys order on crossing $\Gamma C$ extended hence the 25.5% alloy is ordered at room temperature although disordered at temperature, while the 23.0% tin alloy is martensitic on quenching. Composition $XY$ is suggested as the point at which a change occurs in the martensite structure.

The effect of the hot working is to push the order line $\Gamma C$ to higher composition between 27.5% and 28.5% tin thus the 586°C. arrest no longer occurs under these conditions as shown by the isothermal curves and the resistance curves on the ternary alloys while the alloys are still ordered on quenching to room temperature. This type of ordering is probably relatively short range with a smaller domain size. Short range order generally results in broad superlattice lines compared with long range order and this fact has been used to calculate domain sizes. In these alloys although the patterns were not ideal, no sharpening of the superlattice lines was observed after annealing as would be expected. Again however, all previous work has been on alloys close to stoichiometric composition where the anti phase boundary
Fig. 6.4. Sketch of Copper tin phase diagram indicating explanation of effects observed - see text.
energy is high and considerable strain distortion results. In these alloys, far from 25 atomic per cent tin, the anti-phase boundary energy will be much lower and therefore, it is suggested, only very limited line broadening would be expected and this is not detectable with these films.

C. The High Temperature X-ray Results.

Although they are far from conclusive evidence the limited high temperature X-ray results on the annealed 26.7% tin alloy do confirm the above hypothesis. That is, this alloy is ordered only at 570°C and disordered at all temperature from 600°C upwards.

D. The lattice parameter of the $\beta$ and $\gamma$ phases.

Previous results had reported a large discrepancy between the lattice parameter of Isawa obtained at 650°C and all other results obtained at both higher and lower temperatures. The high temperature results obtained in this research agree reasonably well with the bulk of the previous work (Fig.6.5).

There is also general agreement between the X-ray parameters obtained on quenched specimens and those obtained by previous workers (Fig.6.5) but the slope of the lattice parameter composition curve on the hot worked alloys is greater than that obtained by all other workers. After the 27.5% tin alloy had been thoroughly annealed its lattice parameter decreased so that the slope of the lattice parameter composition curve agreed with previous workers.

A similar change in the slope of the lattice parameter
Current research

- As received - hot rolled at 600°C
- Annealed at 600°C
- Measured at 700°C

All values corrected, where necessary, to Å

Fig. 6.5. A comparison between the lattice parameters of the β phase obtained in this research and those of other workers.
composition curve has been observed in iron silicon alloys when these alloys form an off-stoichiometric Fe₃Si ordering,\textsuperscript{59} which has an identical D₀₃ type superlattice. This presents more evidence for the ordering of the 27\% alloy after hot working and further indicates that the 25\% tin alloy is disordered and unaffected by hot working.
Electrical Resistance measurements on quenched specimens were initiated to further elucidate the high temperature reaction in these alloys, as it has been shown that it is the residual resistance which decreases during long range ordering while other factors, notably the temperature coefficient of resistance may increase or decrease according to the particular system leading to some anomalous results at high temperature. A knowledge of the residual resistivity may be obtained from the resistivity at room temperature, together with the temperature coefficient of resistivity, but to obtain this implies that the high temperature structure is capable of retention unchanged at room temperature. Although this was thought to be possible the present X-ray results indicate that the structure always contains some martensite at room temperature and also that the structure is thought to order even on quenching. Because of the high temperatures involved (relative to the melting point) in heat treating these alloys there will also be a significant number of vacancies present of which a certain proportion may be retained by quenching.

The effects of all these variables on the resistivity of these alloys is not known, nor is the cumulative effect of each on the other, so that, short of extensive postulation, these results have little significance and are only reported for completeness.

However, aside from the main issue, a few points worthy of further mention have emerged. It seems probable that at least
a percentage of the vacancies present at temperature are retained by the quenching as the results of the 25.6 tin alloy show. On ageing this alloy at room temperature for 16 hours there is a resistance increase of approximately 1.5%. This increase could be associated with the diffusion of vacancies in copper and metals of similar melting point to dislocations and sessile rings as is reported by Broom at times and temperatures comparable to those found here. It has also been observed that if these alloys are quenched and then immersed directly into liquid air a considerable proportion of martensite forms but if they are allowed to age prior to liquid air treatment very little martensite forms so that vacancies are also associated with the ease of martensite formation.
SECTION V  The Binary Copper Tin Phase Diagram

It is necessary, in the light of the results reported here and elsewhere, to consider the final form of the copper tin phase diagram. It has been shown that the $\beta/\gamma$ transformation involves ordering and it is now necessary to consider how this is related to:

(i) The $(\beta+\gamma)$ two phase region
(ii) The 536°C arrest.
(iii) The 755°C 'peritectic'

(i) The $(\beta+\gamma)$ two phase region

The existence of a two phase field between ordered and disordered regions has swayed for and against for many years. That two phase order plus disorder regions do occur there is little doubt as exemplified by the $(\beta+\beta')$ field in the Copper Beryllium system and the $(\beta+\gamma)$ field in the ternary alloys investigated here. However, in the binary alloys no similar phase is observed. It could, of course, be suggested that it is very narrow and so is never detected. Two phase regions have been suggested without microscopic evidence, for example as a result of electrical resistance work on Cu Zn and Cu$_2$ Au alloys but later work on Cu$_3$ Au indicates that the two phase region may involve the formation of a modified ordered structure, not an ordered plus disordered region.

However, in these alloys we have, as a comparison, a microscopic two phase region in one alloy containing 26.5% tin 0.5%
nickel but no two phase region in a 26\% tin alloy under the same condition of test although both alloys have the same crystal structures and transformation characteristics. Again as the nickel content of these alloys is decreased the field becomes narrower and extrapolation indicates that it would become a line with zero nickel content. All the facts indicate a line transformation from $\beta \rightarrow \gamma$ in the binary alloys while the two phase region is observed in the ternary alloys because of the partition of nickel between the ordered and disordered regions as shown by microprobe analysis.

The position of the line has not been shown directly by any of the results obtained. Mendus and Knodler\textsuperscript{19} have stated that ordering decreased at 25\% tin at 700°C. A first approximation of the position of the $\beta/\gamma$ change is obtained by extrapolating the two phase field from the ternary alloys while the specific heat measurements of Hamusumi and Odamura\textsuperscript{12} are the only direct observations. However, Hamusumi and Odamura report the 'peritetic' reaction 10°C lower in temperature and 1/\% too high in tin content compared with the currently recognised values\textsuperscript{1, 48}. If their results are modified by this amount a fair estimate of the position of the $\beta/\gamma$ reaction is obtained which agrees well with the ternary extrapolation.

(ii) **The '596°C. arrest'.**

The thermal arrest observed in alloys with from 16\% - 25\% tin
at 586°C has been shown to be caused by a large precipitation of α. This is brought about by the ordering of the β phase and the reaction may be represented in terms of free energy changes as shown in Fig. 6.6; that is because of the ordering the γ phase of higher tin content has a lower free energy and so α is rejected to obtain a lower free energy mixture.

(iii) The 755°C 'peritectic'

The reaction occurring on solidification at 755°C has been interpreted as a peritectic reaction almost solely as a result of thermal analysis curves on which an arrest is detected at this composition. A determination of the solidus by quenching has shown that this is a smooth curve and not consistent with a peritectic reaction. Additionally Hamasumi and Takamoto20 have measured electrical resistance changes during both melting and solidification and their results are reproduced in Fig. 6.7. They have interpreted their curves as a peritectic but it is suggested this cannot be the case. Fig. 6.8 indicates the curves expected, under equilibrium, if the reaction were a peritectic. While non-equilibrium effects could account for many of the discrepancies between the two curves on Figs.6.7. and 6.8. the start of the reaction on heating on curves (Fig.6.7.) numbered 4, 5, and 6 at 736°C., 735°C. and 731°C. respectively, is in no way accountable by a peritectic reaction at 742°C. as they suggest. A sloping curve followed by an arrest would be expected as shown in Fig.6.8.
Fig. 6.6. Schematic diagram of the possible free energy changes accompanying the $\beta$ to $\gamma$ transformation.
However, the curves obtained in Fig. 6.7 are possible if the alloys were disordering and melting at one and the same time; while above and to the left of the peritectic line which corresponds to T₀ the solid has no long range order and so melting proceeds in a conventional manner. Conversely during solidification ordering gives rise to the heat arrests measured, the size of which are probably magnified by the general upward sweep of the solidus at slightly higher tin content. This upward sweep being a further indication of the increased stability of the γ phase brought about by the ordering.
Fig. 6.7. The electrical resistance temperature curves obtained during melting and solidification by Harasumi and Takamoto and their derived phase diagram.

Fig. 6.8. Equilibrium resistivity temperature curves expected from the above peritectic reaction.
SECTION VI  The effect of nickel on the conductivity of the eutectoid

During the determination of the resistivity temperature curves for the nickel containing alloys it was observed that, whilst there is a resistance decrease during the \((\alpha+d) \rightarrow \gamma\) eutectoid of the binary alloys, there is a resistance increase in the ternary alloys. The addition of one atomic per cent nickel decreases the resistance of the 26\% tin alloy at 500°C from 42 micro-ohms / c.m.\(^3\) to 32 micro-ohms / c.m.\(^3\). As the resistance of both the \(\beta\) or \(\gamma\) and \(\alpha+\beta\) or \(\gamma\) structures in the nickel containing and nickel free alloys are comparable this decrease must be due to a change in the resistivity of the \(\delta\) phase. All these alloys have a similar eutectoid \((\alpha+d)\) morphology in which \(\delta\) is the continuous phase (Fig.3.21 and 4.14) and therefore is the major factor in deciding the resistance of the alloy.

The temperature coefficient of resistivity of the nickel containing \(\alpha+\delta\) is also higher than the temperature coefficient of the binary alloy which indicates that the resistivity of nickel containing \(\delta\) is probably still lower at low temperatures assuming no anomalies in the resistivity temperature curves.

An alloying addition which causes a decrease in the resistivity of an alloy is unusual. Although the evidence is limited it is useful to discuss the possible reasons for the decrease observed.
There are many factors which affect resistivity but generally they tend to increase it, however, a decrease could be caused by an increase in purity, a decrease in the disorder of the lattice thereby increasing the mean free path of the electrons or by increasing the number of conduction electrons themselves.

(i) Alloy purity.

Although no specific check has been made on the resultant purity of the alloys, high purity materials were used for both the binary and ternary alloys, so that any increase in purity of the nickel alloys must result from the nickel "mopping up" any deleterious elements. Nickel is not an element which is normally used for this purpose.

(ii) Crystal Structure

The $\delta$ phase has a structure similar to the $\gamma$ brass cubic structure except that the unit cell is doubled and there are 416 atoms per unit cell instead of 52$^6$. The atomic arrangement is ordered$^6$. Bash and Upthegrove have suggested that the addition of nickel causes the structure to become tetragonal or hexagonal. This was on the basis of extinctions observed under polarised light but similar experiments on the present alloys did not confirm this. However, the addition of some ternary elements to $\delta$ does cause hexagonality$^4$ (Ref. Chapter I Section III). X-ray powder patterns of the ternary alloys do contain extra lines compared with the binary patterns$^6$ but this work has not been analysed.
However, none of these changes would be expected to cause the resistivity decrease observed.

Further examination of the \(\delta\) structure shows that it is basically B.C.C. but with 16 atoms / unit cell missing and an atomic re-arrangement to take up the vacant sites. It could be suggested that the nickel fits into these pseudo vacant sites and simplifies the structure giving increased conductivity. This would also account for the greater ductility of the nickel containing alloys. However, if this were so one would expect 2 atomic per cent nickel to further decrease the resistivity and this is not so.

(iii) Electronic Changes

The conductivity of an alloy is also associated with the freedom of electrons to be easily excited into higher energy levels in the density of states curves and therefore with partially filled Brillouin Zones. Brass type structures have room for 1.70 electrons / atom in their first Brillouin Zone but CuSn has only 1.63 electrons / atom and so should not have a higher resistance because of this. Further, reference to the copper zinc system, which has a wider \(\delta\) phase field, shows that the resistivity maximum is at an electron atom ratio of 1.60 although the phase exists to an electron atom ratio of 1.70 so that other factors appear to override the effect of the conduction electrons.
However, nickel has been shown to have an effective valency of zero in some electron compounds and could be considered to be an electron accepter thereby increasing the freedom of the conduction electrons.

No definite conclusions can be drawn regarding the effect of nickel on the resistivity of the $\delta$ phase but further X-ray and low temperature resistivity work should indicate whether these hypotheses have any merit.
CONCLUSIONS

The ordering of the $\beta$ phase, observed by Hendus and Knodler\textsuperscript{19}, has been confirmed and associated with the $\beta$ to $\gamma$ transformation. The exact position of the ordering has not been defined, but a fair approximation obtained as a result of the work on ternary copper-tin-nickel alloys. No experimental evidence has been obtained which confirms the existence of a two phase ($\beta + \gamma$) field in the binary alloys and it is concluded that there is no justification for a phase boundary in these alloys. The addition of nickel however, does result in the appearance of a two phase ($\beta + \gamma$) region as a result of partition of the ternary element between the ordered and disordered regions.

It is suggested that the ordering causes the '586°C. arrest' which manifests itself as a precipitation of $\alpha$ and ordering is also responsible for the thermal arrest previously interpreted as the 755°C 'peritectic'. Previous results can be accounted for in the light of these interpretations. The ordering reactions cannot be suppressed by water quenching, and if the ($\alpha + \delta$) eutectoid reaction is prevented, ordering occurs during cooling in alloys of lower tin content than are ordered under equilibrium. The hot working of 26% and 27% tin alloys (but not the 28% tin alloy) causes disordering but the hot worked alloys also order on quenching.

The temperature at which martensite starts to form on quenching these alloys is higher than suggested by Kurdjumov\textsuperscript{17}.

It has been shown during isothermal experiments that the transformation product formed below approximately 400°C probably
contains some ($\gamma + $) and this indicates that the temperature reported
for the $\delta$ to ($\alpha + $) eutectoid may be too low. The addition of nickel
increases the temperature at which the $\xi$ phase is first observed thus
indicating an increase in stability of the $\xi$ phase and making previous
research on the copper-tin-nickel phase diagram, which does not include
the $\delta$ to ($\alpha + $) eutectoid reaction, very doubtful.

The binary copper-tin phase diagram has been modified as shown
on Fig. 7.1. It is suggested that the phase fields should be
relabelled as shown to bring them into line with the lettering used
in other copper base systems.
Fig. 7.1. The modified copper tin phase diagram

The lettering refers to that used on Fig. 1.1.
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