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THE SYSTEMS SILVER-INDIUM AND
SILVER-INDIUM-ALUMINIUM

by

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TO MY WIFE

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ABSTRACT

In the system Ag-In the isothermal phase transformation at 287°C claimed previously by Weibke and Eggers does not exist. Metastability of the γ -phase and the indium-phase at room temperature is persistent. The boundaries of the intermediate phases have been redetermined. At room temperature the equilibrium γ -phase (hexagonal) exists between 71.0 and 70.3 wt. per cent silver, and has the cell dimensions $a = 2.961 \pm 0.002 \text{ \AA}$, $c = 4.778 \pm 0.004 \text{ \AA}$. At 325° and higher temperatures the γ -phase region extends to higher indium concentrations than given by Weibke and Eggers. The order-disorder transformation of the γ -phase postulated by Hellner does not exist. The γ -phase undergoes a metatectic phase-reaction at 205°C.

At high temperatures the liquidus lies approximately 8°C higher than that determined by Weibke and Eggers.

At room temperature the ϵ -phase exists between 67.5 to 65.0 per cent silver. At these compositions the cubic cell edges of the ϵ -phase are $a = 9.878 \pm 0.004 \text{ \AA}$, $a = 9.887 \pm 0.004 \text{ \AA}$ respectively. The $\gamma/(\gamma + \epsilon)$ boundary has been redetermined and extended. The order-disorder transformation of the ϵ -phase claimed by Weibke and Eggers does not exist. The heat effects ascribed to this transformation were shown to be due to $\gamma \rightarrow \epsilon$.

A new α' phase is claimed to exist at approximately 73.8 wt. per cent silver. It is formed by a peritectoid phase reaction at 187°C. In the α' -phase the silver atoms occupy the face-centered positions and the

indium atoms the corner positions of the cubic lattice. The intensities of diffraction lines were calculated using such a model, and were qualitatively in good agreement with the observed intensities of the α' -phase. The cell edge of the α' -phase is $4.144 \pm 0.004^{\circ}$ Å at room temperature which is the same within experimental error as that of the α -phase.

Indications are that the ϕ -phase has a composition of a few tenths of a per cent silver higher than that given by Ag_2In .

A new phase diagram of the system Ag-In was constructed.

In the ternary system Al-In-Ag, a number of alloys were examined and a room-temperature isothermal section was constructed. Isothermal sections were also constructed at 143°C and 148°C . A room temperature section giving the region of metastability in the ternary system was constructed. Three Vertical Sections were obtained by D.T.A. showing that invariant phase-transformations occur at 143°C (ternary eutectic), 148°C , 205°C , 241°C , 506°C ; the latter are ternary peritectic transformations. The high temperature β -phase of the binaries Ag-Al, and Ag-In forms a single-phase region in the ternary system, i.e. the two binary phases Ag_3Al (β) and Ag_3In (β) are miscible in all proportions forming a single phase.

Some evidence indicates that the μ -phase of the system Ag-Al is not of the β -Manganese type, but is primitive cubic with a cell edge of $a = 4.051^{\circ}$ Å. Further work is required on this point.

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INTRODUCTION

Before any measurements can be made of particular properties of individual alloy phases the range of homogeneity of phases must be established as a function of composition and temperature. In theoretical discussions, reference is usually first made to the stability of phases. Thus, directly or indirectly, equilibrium phase-diagrams of alloys are of fundamental importance. Although a number of "rules" have been established which can "predict" to some extent the occurrence of certain phases, no complete theory of alloys exists which would make the construction of phase-diagrams a purely theoretical problem. It is conceivable that with present-day high-speed electronic computers the pertinent differential equations, based on the known laws of quantum mechanics, could be solved for an alloy system, but, no structure of a compound of any complexity has been predicted successfully, as yet, on the basis of atomic parameters and quantum mechanics, let alone a complete phase diagram. The construction of phase-diagrams is still largely dependent on experiment.

THE NATURE OF THE PROBLEM

The object of the present investigation was to establish the equilibrium phase-diagram of the system Silver-Indium in detail, and to determine to some extent the phase-diagram of the ternary system Silver-Indium-Aluminium.

Although the system Silver-Indium has been studied previously (29,30,61) the findings contradict each other to a considerable degree in the composition range of 23-40 wt. per cent indium. Both published phase diagrams which are reproduced in Figs. 1 and 2, show some conflict with "phase rule". Except for the terminal α -phase, the boundaries of the intermediate phases were not established with any accuracy. The other two contiguous binary systems, "Aluminium-Silver" and "Indium-Silver" are considered to be well established. In particular, the less complex system, "Aluminium-Silver", has been extensively investigated in the past by many people, as discussed under "The Binary System Aluminium-Silver". An investigation of a ternary system, is obviously more laborious and time consuming. Understandably, a detailed investigation of the ternary system was not possible within the given time. With respect to the ternary system my aim was to establish a ternary diagram of a general nature.

Two systematic methods can be used to determine a complete ternary phase diagram: the "isothermal section" method and the "vertical section" method, with the latter method being predominantly used in the present investigation. Not all phase boundaries could be based directly on experimental data, but I deduced them by applying the "phase rule" and interpolating available experimental data.

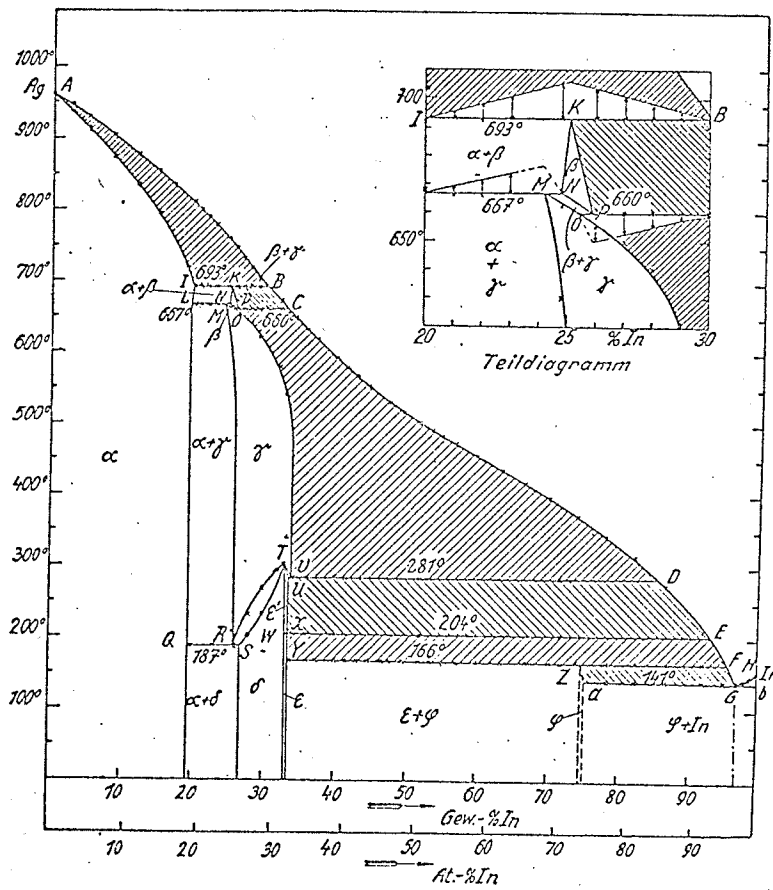


Fig. 1. The System Ag-In

by Weibke and Eggers (61)

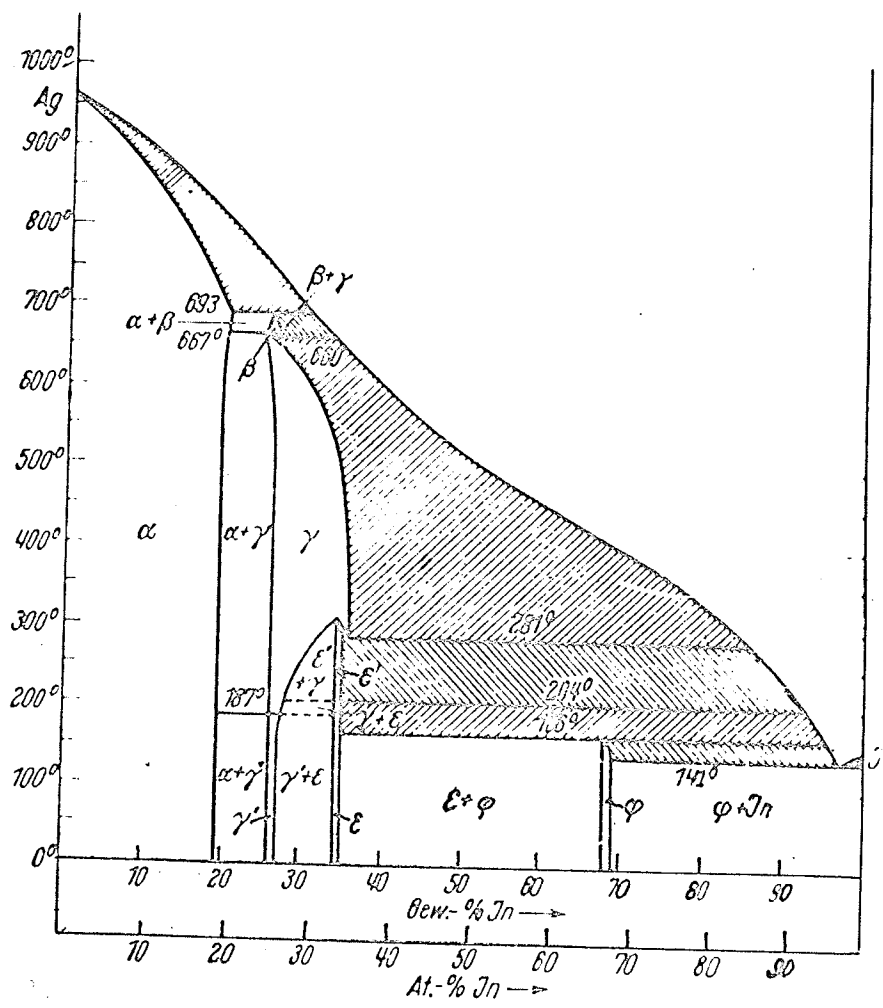


Fig. 2. The System Ag-In
by Hellner (30)

A complication which is usually encountered to some degree in phase-equilibria studies is metastability. In the present investigation this phenomenon was particularly persistent within a certain composition range, at lower temperatures, due to the presence of relatively low transformation temperatures in this system. It was apparent that equilibrium could not be established within a reasonable length of time. I realized that the presence of a metastable phase in addition to the stable phases in a ternary system would yield very complex x-ray diffraction patterns which would be very difficult to interpret unambiguously. It was for this reason that I did not use the latter method of identifying phases in the ternary system. Photomicrography on the other hand could be used to identify phases in the ternary system, because it was found that the etching colours of the different phases established for the binary systems were practically the same in the ternary system.

To a limited extent, the ternary system "Aluminium-Indium-Silver" has been investigated previously. Campbell and Wagemann (72) determined the ternary "miscibility gap" and the liquidus (71). Except for this work the ternary system has received no further attention.

THEORETICAL CONSIDERATIONS

Thermodynamic Approach

At constant pressure the equations relating composition and temperature of phases along a line of equilibrium in a binary system are as follows:

$$(1) \quad \left(\frac{dx_2^\alpha}{dT} \right)_{P, \text{ coex}} = \frac{(1 - x_2^\beta) \Delta h_1 + x_2^\beta \Delta h_2}{T (x_2^\alpha - x_2^\beta) \left(\frac{\delta^2 g}{\delta x_2^2} \right)^\alpha}$$

$$(2) \quad \left(\frac{dx_2^\beta}{dT} \right)_{P, \text{ coex}} = \frac{(1 - x_2^\alpha) \Delta h_1 + x_2^\alpha \Delta h_2}{T (x_2^\alpha - x_2^\beta) \left(\frac{\delta^2 g}{\delta x_2^2} \right)^\beta}$$

Where "g" is related to the chemical potential " μ " as shown next. "x" is the mole fraction, and "T" is the absolute temperature. The Greek superscript indicates the phase (it is not an exponent) while the Latin subscript indicates the species. $\Delta h_1 = (h_1^\beta - h_1^\alpha)$; $\Delta h_2 = (h_2^\beta - h_2^\alpha)$ i.e. Δh_i is the heat of transition of one mole of substance "i" from phase " α " to phase " β ". In general Δh_i and $\frac{\delta^2 g}{\delta x_2^2}$ are functions of temperature and composition where

$$\left(\frac{\delta^2 g}{\delta x_2^2} \right)^\alpha = \frac{1}{-x_2^\alpha} \left(\frac{\delta \mu_1}{\delta x_2} \right)^\alpha$$

$$\left(\frac{\delta^2 g}{\delta x_2^2} \right)^\beta = \frac{1}{x_1^\beta} \left(\frac{\delta \mu_2}{\delta x_2} \right)^\beta$$

and μ_i^α and μ_i^β are the chemical potentials of substance "i" in phase " α " and phase " β " respectively. The differential equations (1) and (2) make it

possible in principle to construct various phase boundaries by integrating with respect to temperature. To do this the functions $\frac{\delta^2 G}{\delta X_2^2}$ and Δh must be known explicitly in terms of temperature and composition and this is generally not the case. Where theoretical calculations of equilibrium curves have been made approximations have been introduced. The most commonly made approximations are: One component being only sparingly or not at all soluble in a phase; consideration of dilute regions only; Δh is treated as independent of temperature in the range of integration; ideal behaviour i.e. $\mu_i = \mu_i^0 + RT \ln X_i$ for one or both components; and truncated Taylor expansions for Δh and μ_i in terms of composition. With such approximations various formulae of limited applicability are obtained which are useful provided certain starting points are known, but which are obviously not valid for the general case and cannot be used to calculate a complete phase diagram without resort to experiment, unless the system is an exceptionally simple one and "well behaved" for the whole concentration region.

Structural Approach

In a binary system of metals "A" and "B" each metal may be capable of incorporation in the lattice of the other metal interstitially or by substitution, to some extent without structural change. The alloy formed in this way is called a terminal solid solution, based on "A" or "B". Interstitial solutions can be formed only when one atom is very much smaller than the other. The small atom which is usually hydrogen, boron, nitrogen or carbon fits into the available spaces in the lattice rather than substituting for other atoms on lattice sites. Pairs of metals which have the same crystal structure may form terminal solid solution for all concentrations e.g. Au - Ag, Cu - Pt, Ni - Mn. A prerequisite for such total mutual solubility to occur is that "A" and "B" must have the same crystal structure but other properties must be compatible as well such as having similar atomic diameters (usually within 15%).

In addition to the terminal solid solutions there may be one or more intermediate phases formed, with structures different from those of the pure components. The composition range of the intermediate phase may or may not include the composition $A_n B_m$ with "n" and "m" being small integers and, the compositions of the intermediate phases may be completely at variance with classical valency rules. In metal systems the intermediate phases sometimes exist over a range of composition. Although there is fundamentally no difference between phases having either wide or restricted variation in composition some writers reserve the term "intermetallic compound" for the latter case when the composition variation is less than

one atomic per cent.

The problem of predicting the resultant structures and their fields of stability, on purely theoretical grounds, when two or more components are melted together has engaged the attention of a number of theoreticians in the past, but no complete solution has been achieved, mainly because many factors determine the structure of alloys some of which are not fully understood.

A set of empirical rules which explained and "predicted" to some extent the occurrence of certain phases in binary alloy systems was set forth in the classical work of Hume-Rothery (7). He stated that the occurrence and stability of a number of phases could be rationalized in terms of three factors:

- 1) The relative size of the two atoms (size factor).
- 2) The relative electronegativity of the two atoms (electronegativity factor).
- 3) The valence electron concentration per atom (v.e.c.) (the electronic factor).

The effect of atomic size on alloy formation was originally formulated as a negative rule, viz: that formation of extensive binary substitutional solid solution is limited to cases where the diameters of the atoms of the two metals do not differ by more than 14-15 per cent (6).

The stability and occurrence of a large number of intermediate phases, the "Laves" phases, are also determined primarily by the relative size of the atoms. These phases are characterized by a very high coordination number, $13\frac{1}{2}$ on the average. Geometrically this corresponds to a

dense packing of spheres of unequal size, and this requires both a limited range of radius ratio $\frac{r_A}{r_B}$ for the two species as well as a specific composition, "AB₂", where "A" is the larger atom and "B" the smaller atom. The ideal radius ratio for dense packing for spheres of unequal size is 1.225. The "Laves" phases can have one of the following structure types: MgCu₂ (cubic), MgZn₂ (hexagonal) MgNi₂ (hexagonal). These three structures are related by stackings of double layers in three different sequences, or they can be viewed as connected tetrahedra with the "B" atoms being located at the corners of the tetrahedron and the larger "A" atom fitting into the space enclosed by the tetrahedron. The three structures differ according to the way in which the tetrahedra are connected, by points, edges, bases, or a mixture of these. The "Laves" phases do in fact usually show a narrow homogeneity range, but not always. Thus the radius ratio of the components can frequently serve as a stability criterion for intermediate phases as well: If the radius ratio is nearly 1.2, the electronegativities of the components nearly equal and the v.e.c. is within certain limits, an intermediate phase, a "Laves" phase, is most likely to form. Which type of "Laves" phase will be formed depends largely on the "electronic factor".

It is well known that the diameter or radius of an element as given by the distance of closest approach in the solid state is not a constant quantity. The size of the atom may vary considerably depending on the element with which an alloy is formed. For example, the atomic sizes defined in terms of the distance of closest approach of the metals Pb, In, and Tl, show a marked change when alloyed with noble metals, relative to the

pure metals. It can be stated that in general the atomic size in the solid state depends on the type of bonding, on the coordination number, and on the atomic size and nature of the other component. In spite of the rather arbitrary definition of atomic size, the "size factor" has been found to be useful as a rough guide to the possible formation of extensive solid solution and the stability of certain intermediate phases.

J.D. Eshelby (1) calculated the limit of stability of a solid solution in terms of relative size of the atoms on the basis of a continuum theory of lattice defects and showed that the stability limit is reached when the relative size exceeds 14% - 15%. Thus, the empirical "size factor" originally proposed by Hume-Rothery does have some theoretical justification.

With reference to the electronegativity factor the reasoning in "predicting" or rationalizing the existence of intermediate phases and the existence of restricted primary solid solution is as follows: The more electropositive one component and the more electronegative the other, the greater is the tendency to form an intermediate phase. Conversely the primary solid solution range becomes more restricted. The homogeneity range of the intermediate phase also becomes more restricted, the more purely ionic the bonding of the intermediate phase with the limiting case being a "line compound" or an "intermetallic compound".

The electronegativity factor is of course the predominant factor involved in the formation of ionic compounds where the difference in electronegativity is sufficiently great to permit electron transfer from the metal to the non-metal with reduction of energy in the system. This transfer,

together with the interaction energy of the system of ions (Coulomb or Madelung energy), is primarily responsible for the formation and stability of the compound. A feature of these compounds is that each ion is surrounded to the maximum extent possible by ions of the opposite charge. The electronegativity factor which operates in such a clear fashion in the alkali halides, is also involved in a similar way in compounds between metals. To give only two examples, Mg_2Pb and Mg_2Sn show a somewhat ionic character. In this case, the more electropositive metal magnesium plays the role of the cation and lead and tin that of the anion. While transfer of charge is not complete there is no doubt that it occurs to some extent. Thus, the relative electronegativities of atoms can indicate qualitatively whether a new phase is likely to form and the nature of the bonding in the new phase. The significance is qualitative only.

The attempt to define electronegativity quantitatively has produced in the past twenty years a large volume of literature on the subject, much of it due to the inherent vagueness of the concept. The original definition by L. Pauling (2): "the power of an atom in a molecule to attract electrons to itself" is obviously only a qualitative definition since the terms in the definition itself are vague. Only two equations from among a dozen or more proposed for calculating or estimating electronegativity values of individual atoms will be mentioned. L. Pauling (2) proposed the equation

$$\left| X_A - X_B \right| = K \Delta^{1/2}$$

where "X" is the electronegativity of the atom indicated by the subscript

and K is a constant ($23^{-1/2}$) if Δ is expressed in e.v. and $\Delta = D_{AB} - \left[(D_{AA})(D_{BB}) \right]^{1/2}$ where "D" stands for the respective bond energies. Pauling's equation yields only differences in electronegativities. To compute individual values, he arbitrarily assigned $X = 2.1$ to hydrogen.

R.S. Mulliken (3) derived the equation $X = \frac{1}{2} (I + A)$ for calculating absolute electronegativities. "I" and "A" are the ionization potential and the electron affinity respectively. Both equations are based on the "valence bond" wave function description of a diatomic molecule. Pauling's electronegativities are proportional but not equal to those of Mulliken, and the two scales differ in their units. Pauling's numbers are in units of one-half power of energy (e.v.)^{1/2} while Mulliken's values are in energy units (e.v.). Pauling's electronegativities presumably represent averages over the range of valence states exhibited by the different elements while Mulliken's values are calculated with "I" and "A" pertaining to the valence state of the atom in a particular compound. It is clear that the electronegativity of an element is not a constant quantity but will vary with the nature of the valence state and this presents an added difficulty when applied to metals and alloys, since the classical valencies of the isolated atoms do not strictly apply in such cases - in particular, the coordination number (number of nearest neighbours) bears no relation to the valency attributable to an isolated atom. Nevertheless, the concept of electronegativity can be usefully applied to metallic systems in a qualitative manner.

The possibility of the occurrence of related phases at similar values of valence electron concentration per atom (v.e.c.) in different alloy systems originated from a study of the β -phases (7) which were the first intermediate phases to be called "electron compounds" (8). They are not compounds in the chemical sense; they exist over a wide range of composition and they may exist only in a narrow range of temperature as for example the disordered β -phase of CuZn which exists only at high temperature. Although the $3/2$ v.e.c. is common among the disordered body centered cubic phases, not all such phases exhibit this ratio; MnNi and Mn_3Zn_2 for example are exceptions. Other intermediate phases, e.g. the γ -brass type (complex cubic) and the ϵ -brass type (close-packed hexagonal), occur in various systems at $\frac{21}{13}$ and $\frac{7}{4}$ v.e.c. respectively. Thus, when other factors do not predominate, stable intermediate phases will exist in a system at a valence electron concentration of $\frac{3}{2}$, $\frac{21}{13}$, $\frac{7}{4}$ respectively if such an electron concentration can be achieved in the system. As with the β -phase, it has become clear that the other intermediate phases too are not as sharply defined in composition as was once believed. In addition to the three structure types mentioned, many other structure types have become known where the composition range of stability seems to be determined mainly by the valence electron concentration per atom. (The "Laves" phases were already mentioned in this connection.) It is characteristic of these types of structure that their composition is dominated by transition elements.

Mention must be made of the important advances made by Mott and Jones (9) who interpreted the electronic factor of Hume Rothery in terms of

filling of Brillouin zones (with electrons) or filling of these zones to the largest inscribed sphere (the "Fermi sphere"). This model was a consequence of the assumption that the perturbing lattice potential interacted weakly with the electrons, and this constitutes a "nearly-free" electron approximation. In the "free-electron" (in a box) model the energy of the electron depends on the square of the wave number and the density of states depends on the square root of the energy of the electrons. In the Brillouin zone model the relationship between the wave number vector ($\vec{k}$) and the electron energy (E) is nearly the same but with regions of discontinuity in the energy (energy gaps) and only in the region of energy near these "energy gaps" does the simple relationship between E and $\vec{k}$ break down and become drastically more complex. In the "free-electron" model it can easily be shown that the density of states, defined as the number of electronic states per unit volume, $N(E)dE$, with energies between E and $E + dE$, is directly proportional to $E^{1/2}$ i.e. $N(E) \sim E^{1/2}$. In the Brillouin zone model there is a sharp rise in the $N(E)$ function with increasing energy over that of the "free-electron" curve, as the energy approaches the forbidden energy range, i.e. as the energy approaches the Brillouin zone boundaries which are related to the real crystal structure and can be derived from it. This model provided a means of relating the electronic density of states, as a function of energy, with real crystal structures. One can visualize that as electrons are added to a system (for example, by adding Zn atoms to copper) a favourable situation exists as long as the density of states as a function of energy is large, but when the density

of states diminishes with an increase in energy or is low as when the Fermi surface is far removed from the Brillouin zone boundary the system would conceivably change to another crystal structure type which had a larger density of states for the same energy range and thus could accommodate the same number of electrons in a system with lower total energy. In this way the v.e.c. numbers $\frac{3}{2}$, $\frac{21}{13}$, $\frac{7}{4}$, were related to the peaks in the $N(E)$ vs. E curves. Hence a given structure is stabilized if there are sufficient delocalized electrons to bring the Fermi surface up to the Brillouin zone boundary. Much work has been done on Brillouin zones and their implications for metals and alloys and there seems to be no doubt that the basic ideas of the theory are correct though details of the theory were not always approached consistently in the past. For example, in computing at what energy a discontinuity in energy should occur in filling the Brillouin zone, whether it should occur at the inscribed sphere (energy increases rapidly with $\bar{K}$ beyond this point) or only when the zone is completely filled was a matter of personal choice. Finally it should be mentioned that more recently direct experimental evidence indicates that the Fermi surfaces in metals and alloys are much more complex geometrically than originally assumed, and this makes the accurate calculation of the properties of alloys a formidable task.

Just as with the atomic radius, the valence electron concentration used in predicting stabilities suffers from some ambiguity. To a first approximation it is given by the usual accepted metallic valencies which are the sum of s and p electrons but, it is not quite certain whether

all the $(s + p)$ electrons in the metal or alloy are delocalized. Friedel (10) has suggested that some of the $(s + p)$ electrons may lie in "Bound states" near the solute nuclei which is another way of saying that the solute atoms are incompletely ionized and that some of the conducting electrons are permanently attracted to the more positively charged nuclei. On the other hand, in order to account for the large decreases in the atomic size of indium, thallium and lead when alloyed with noble metals Hume-Rothery and Raynor (11) suggested that these metals are incompletely ionized in the pure state but are completely ionized when dissolved in copper, silver and gold. It now seems unlikely that complete ionization of a polyvalent solute would occur in solid solution. There seems to be no a priori reason why incomplete ionization should occur in indium, thallium or lead and yet be absent in, say, germanium, tin, arsenic or antimony whose atomic sizes do not seem to show abnormal decrease on alloying. To fit into the scheme of the Hume-Rothery rules transition elements were assigned a valency of zero, though occasionally the total number of electrons outside the "inert core" i.e. $(s + p + d)$ have been used to denote the electron concentration (12). Raynor (13), on the basis of studies of chromium and manganese in aluminium, concluded that these transition elements were not contributing to the sea of delocalized electrons but instead were withdrawing electrons to fill their d-shells. The whole chemistry of the transition elements emphasizes their tendency to act with variable valencies, not merely in different alloys but in different composition

ranges of one alloy system, as in the system nickel-zinc, for example, where nickel appears to act with zero valency in some parts of the system and with higher valency in other composition ranges.

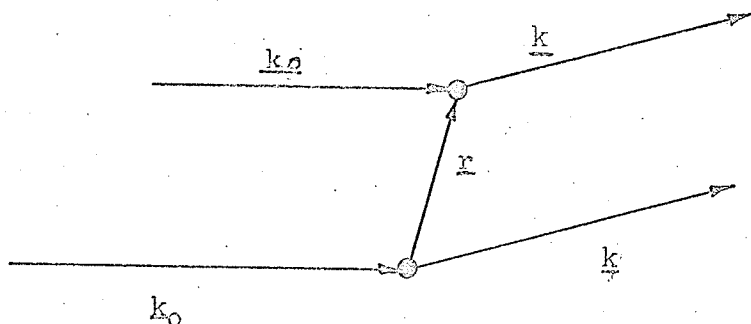
Despite the quantitative uncertainty of the valence electron concentration, electronegativity and atomic size, the Hume-Rothery rules proposed over thirty years ago have been found very useful in rationalizing phase stability from a structure point of view. These empirical rules were strikingly put to the test by Waber et al (14) who showed, considering only the size factor that for 619 binary alloy systems where the difference in atomic size between components is greater than 15 per cent, ninety per cent of these systems exhibited very limited solid solubilities, and for 804 systems where the size difference is less than 15 per cent, fifty per cent of these systems exhibited extensive solid solution.

X-Ray Diffraction

A beam of x-rays (which are electromagnetic waves), falling on an assemblage of periodically arranged atoms (scattering centres) will interact with the electron shells of the atoms and will thereby be scattered. Elastic scattering (scattering without energy loss and so without change in λ) is the important process here; effects such as polarization and absorption are not of major importance for elastic scattering, although the intensity formulae must be corrected for these effects. Each scattering centre can thus be regarded as the origin of a scattered wave (or wavelet) which can be represented by a vector. The scattered waves will interfere (or combine) with each other. A discussion of diffraction therefore requires a technique for studying the combination of wave motions.

A plane wave (ψ) travelling in an arbitrary direction $\underline{r}$ can be written as $\psi = A \exp. i (\underline{k} \cdot \underline{r} - \omega t)$. For the analysis of diffraction effects, only the mutual phase shifts of the waves produced by scattering and interference and not the time course of the waves are of importance; the time factor (ωt) is omitted.

Consider two arbitrary scattering centres which are part of a regular assemblage of n centres on a lattice. The origin ($\underline{r} = 0$)



is placed at one of the scattering centres. For the sake of simplicity, initially the scattering power f (atomic scattering factor) is assumed to be the same for both centres. The initial wave is specified by the vector $\underline{k}_0$ (having amplitude $A = 1$), the scattered wave is specified by the vector $\underline{k}$, and the position of the scattering centres by the vector $\underline{r}$. The resultant wave $F(\underline{k} - \underline{k}_0)$ is given by:

$$F(\underline{k} - \underline{k}_0) = f e^{i(\underline{k} - \underline{k}_0) \cdot \underline{r}}$$

where $(\underline{k} - \underline{k}_0) \cdot \underline{r}$ is the path difference of the scattered waves at $\underline{r}$ and $\underline{r} = 0$ in the direction $\underline{k}$. Since only elastic scattering is considered $|\underline{k}| = |\underline{k}_0| = \frac{2\pi}{\lambda}$ where λ is the wave length of the incident and scattered radiation. Let the translation periods of the regular lattice be a, b, c , in the directions $\underline{a}, \underline{b}, \underline{c}$ respectively, where $\underline{a}, \underline{b}, \underline{c}$ are base vectors of the rectangular coordinate system. $\underline{r}$ can be expressed in rectangular coordinates as $\underline{r} = \underline{a} X + \underline{b} Y + \underline{c} Z$. Then

$$\begin{aligned} (\underline{k} - \underline{k}_0) \cdot \underline{r} &= X(\underline{k} \cdot \underline{a} - \underline{k}_0 \cdot \underline{a}) + Y(\underline{k} \cdot \underline{b} - \underline{k}_0 \cdot \underline{b}) + Z(\underline{k} \cdot \underline{c} - \underline{k}_0 \cdot \underline{c}) \\ &= X \frac{2\pi}{\lambda} (\cos \nu_a - \cos \bar{U}_a) + Y (\cos \nu_b - \cos \bar{U}_b) \frac{2\pi}{\lambda} \\ &\quad + Z \frac{2\pi}{\lambda} (\cos \nu_c - \cos \bar{U}_c) \end{aligned}$$

where $\cos \nu_a, \cos \nu_b, \cos \nu_c$ are the direction cosines of $\underline{k}$ and $\cos \bar{U}_a, \cos \bar{U}_b, \cos \bar{U}_c$ are the direction cosines of $\underline{k}_0$. In the regular array of scattering points only in certain directions will the resultant wave not have zero amplitude.

It can be shown (Buerger, 15) that for a lattice with translation periods a, b, c only in directions for which the conditions

$$(\cos \nu_o - \cos \bar{U}_a) = \frac{h\lambda}{a}$$

$$(\cos \nu_b - \cos \bar{U}_b) = \frac{k\lambda}{b}$$

$$(\cos \nu_c - \cos \bar{U}_c) = \frac{l\lambda}{c}$$

are satisfied simultaneously will the resultant amplitude not be zero, where h, k, l are all integers and the resultant amplitude for such directions is given by

$$F(X, Y, Z) = f \exp i2\pi\left(\frac{Xh}{a} + \frac{Yk}{b} + \frac{Zl}{c}\right),$$

or using fractional coordinates (x, y, z) which have as unity the corresponding lattice translation period, i.e. $x = \frac{X}{a}, y = \frac{Y}{b}, z = \frac{Z}{c}$ the last equation becomes

$$F = f \exp i2\pi(xh + yk + zl)$$

This equation can be generalized to apply to scattering centres where each centre has a different scattering power f_j

$$\text{i.e. } F = \sum_j^{n-1} f_j \exp i2\pi(hx_j + ky_j + lz_j)$$

The equation is usually given in the form

$$F_{hkl} = \sum_j f_j \cos 2\pi(hx_j + ky_j + lz_j) + i \sum_j f_j \sin 2\pi(hx_j + ky_j + lz_j)$$

Letting $\cos 2\pi(hx + ky + lz) = A$

and $\sin 2\pi(hx + ky + lz) = B$

$$F = \left(\sum_j f_j A_j \right) + i \left(\sum_j f_j B_j \right)$$

If the space group contains a centre of symmetry and if the origin of coordinates to which the positions of the atoms are referred is taken at the symmetry centre then it can be shown that $(\sum_j f_j B_j) = 0$ and $F = \sum_j f_j A_j$. This will be the case for the large majority of crystals.

In all but the unsymmetrical space group "P1" an atom in a general position is accompanied by other atoms having symmetrically related coordinates. On the summation $(\sum_j f_j A_j)$ there are groups which not only have common values of f_j (because symmetrically related atoms are identical) but also have related coordinates which permits consolidation of the summation by the rules of trigonometry or exponential combination. The consolidation is performed in terms of the symmetry factor S . If the space group relates a set of "m" points in the general position, the symmetry factor "S" is defined as the wave scattered by a set of unit scatterers located on these "m" points. "S" has the form $\sum_{j=1}^m e^{i2\pi(hx_j + ky_j + lz_j)}$ where the coordinates x_j, y_j, z_j are now related by symmetry, depending on the particular space group. All the symmetry factors for the various space groups have been derived and compiled (53). (F_{hkl}) the structure factor can then be written as $F_{hkl} = \sum_{j=1}^p f_j S_j$ where the summation is now only performed over the "p" different sets of equivalent atoms, which is a great simplification.

The intensity of a wave is proportional to the square of the amplitude i.e. $I_{hkl} \propto (F_{hkl})^2$ where I is the intensity and "F" is the amplitude generally called the "structure factor". Various correction factors have

to be applied to the proportionality before it can be written as an equality; such as the "geometric" factor, the polarization factor and the multiplicity factor.

In the powder diffraction method small crystals are in random orientation and there will always be a plane in the proper orientation for Bragg reflection as the sample rotates, but only a fraction of the volume will be in a reflecting position. The energy of the reflected radiation will be constant with " θ " (disregarding multiplicity), but the energy of the Debye ring will vary with θ since the Debye rings get progressively larger with increasing θ (to 45°). This "geometric" factor correcting the intensity for this effect is $1/\sin^2\theta \cos \theta$. In the usual x-ray diffraction experiments the x-ray beam is unpolarized, but becomes polarized after reflection at the angle " 2θ " which has the effect of reducing the intensity of the scattered (reflected) beam by a factor $\frac{1 + \cos^2 2\theta}{2}$. These two factors are usually combined into one with the form

$$\frac{1 + \cos^2 2\theta}{\sin^2 \theta \cos \theta}.$$

The relative effect of temperature and absorption on the intensity is small and is often neglected.

An important factor that must be considered is the multiplicity factor (p). In the Debye-Scherrer powder method a diffraction line of indices hkl is produced by reflection on all the crystal planes having the same spacing, or by all the planes $\{hkl\}$. The number of lattice planes which are equivalent for reasons of symmetry is called the multiplicity factor (p) and it depends on the symmetry of the crystal and on the indices hkl . Since the reflections of different sets are independent of one another and will contribute equally to the "diffraction ring" it is obvious that with several different sets of planes diffracting to the same area on the film the intensity on that area will be greater than it would be if only one set of planes contributed, and a correction has to be applied which is " p ".

With the correction factors applied to F_{hkl}^2 the intensity of a diffraction line in the powder method is given by

$$I_{hkl} = K F_{hkl}^2 \left[\frac{1 + \cos^2 2\theta}{\sin^2 \theta \cos \theta} \right] p$$

Various other factors which only have a small influence have been neglected.

" K " is a constant for a given constant set of experimental conditions. It can be determined by a standardization procedure or, if only relative intensities are of interest, it can be assigned an arbitrary value.

The final equation arrived at here, relating the intensity and the structure factor will be used later in calculating some intensities.

CONSIDERATION OF METHODS AND TECHNIQUES

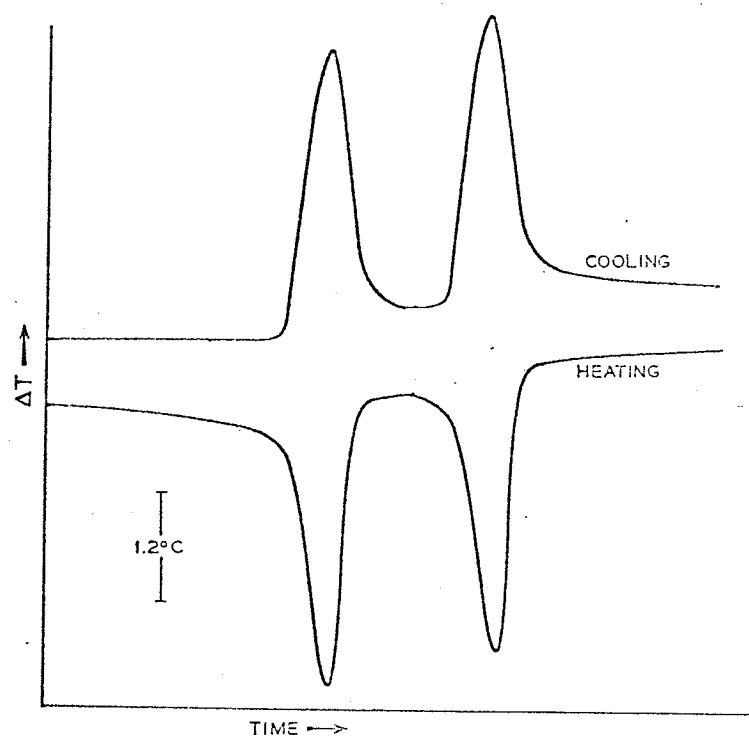
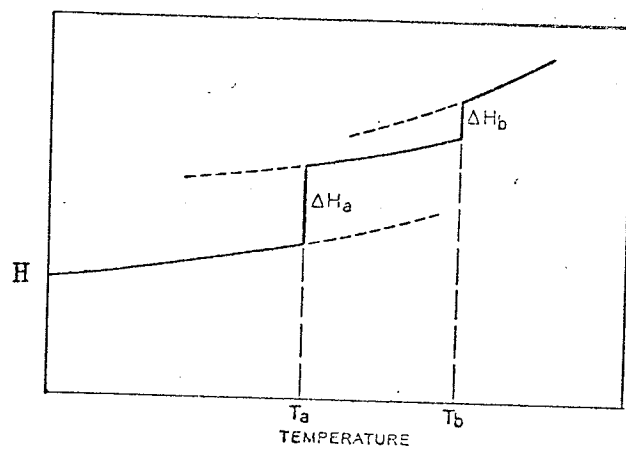
Differential Thermal Analysis

The basic principles of differential thermal analysis (D.T.A.) are well-known. A profusion of literature on this subject exists, and a number of excellent books on the theory and the application of D.T.A. are available, only two of which will be mentioned(73,74). Therefore, I shall only state very briefly the general principle upon which D.T.A. operates, and shall give more detailed consideration to some particular aspects of D.T.A. which are pertinent to the present investigation.

Differential thermal analysis is a technique by which thermal effects are measured, usually as the sample is heated or cooled.

Any material has a free energy, $G = H - TS$ where the symbols have the usual meaning - "H" is the heat content or enthalpy, "T" the temperature, and "S" the entropy. The system will tend to reach whichever of the possible states has the least free energy. If for example the material is crystalline and it is taken to a temperature at which another structure has a lower free energy it will tend to change to the more stable structure with an accompanying change in H. The change to a lower "G" might be via a chemical reaction, melting, or boiling etc. "H" is in general a function of temperature and does not remain constant with temperature, but at the transition to a more stable phase the change in "H" is discontinuous as shown in Fig. 3, at T_a and T_b .

When the difference in temperature between the sample and an inert reference body is measured as a function of temperature as the sample



Differential Thermal Analysis Curves Showing Two Transitions

Fig. 3

and the reference body (which are in close proximity) are heated (or cooled) the temperature difference is nearly zero (if the reference body is suitably chosen), until T_a (or T_b) is reached. At this time the temperature of the reference body continues to rise or fall but the temperature of the sample remains nearly constant since the change in H occurs at constant temperatures, and the observed difference in temperature will not be zero. After the transformation is complete the difference in temperature will again become nearly zero, as shown in Fig. 3 which is a typical differential thermal analysis graph.

A number of commercially available instruments are satisfactory for many applications. They are quite sensitive to small heat changes and require only small samples (mgm - range) and this is achieved by bringing into direct contact the sample and the sensing device, usually a thermocouple. In the analysis of metals and alloys direct contact between sample and thermocouple junction must be avoided because of mutual contamination at elevated temperatures. Thermocouple shields of "alundum" or other refractory material into which the electrically insulated thermocouple wires are inserted must be used, and this results in some loss of sensitivity. The D.T.A. apparatus used in the present investigation was designed and built to have sufficient sensitivity to detect even small heat changes in alloy systems such as occur in solid-solid transformations.

Depending on the thickness of the shielding material and its thermal conductivity the time lag of response and the total mass of the

sensing device will be increased relative to an unshielded thermocouple. Consequently, larger samples must be used to obtain well-defined "peaks". Certain problems are inherent in the use of larger samples, the main problem being the finite time an advancing temperature front requires to permeate the sample. Consequently, the sample geometry becomes an important factor. The proper shape for a sample is one that permits a uniform flow of heat from and to the sample implying that the sample be highly symmetrical in the direction of the temperature gradient. A cylindrical sample (using a cylindrical furnace) with the thermocouple placed at the center of the cylinder satisfies these requirements. When a thermocouple shield is inserted in the cylindrical sample, the sample becomes a tube. It is desirable that the wall thickness of the sample (tube) and the shielding tube be small, though in the latter case one is technically limited to approximately 1.5 mm. wall thickness if the material is pure aluminum. It is evident that it is necessary to strike a compromise between sample size and sample thickness for a given dimension of shielding tube if the sample is not to extend greatly in length. If the sample wall is relatively thin a reaction front will require less time to traverse the sample and the resolution of closely spaced peaks is increased. If the heating or cooling rate is very slow and the sample and the reference thermocouple are situated in close proximity in the same metallic block, the heat exchange between the sample and the reference thermocouple may be too rapid, relative to the time required for the reaction front to traverse the sample, and the

full heat effect is not utilized; then an insulating sleeve placed around the sample can increase the sensitivity of the thermocouple to small heat changes. These were some of the factors which had to be considered in achieving the objective. Since the commercially available gases contained some oxygen a vacuum and purification system was constructed which made it possible to perform analysis either in vacuo or under inert atmosphere.

The apparatus was designed primarily to be operated at a fixed heating and cooling rate, though some non-mechanical flexibility was conveniently achieved with the variable transformer supplying the "Power stat" .

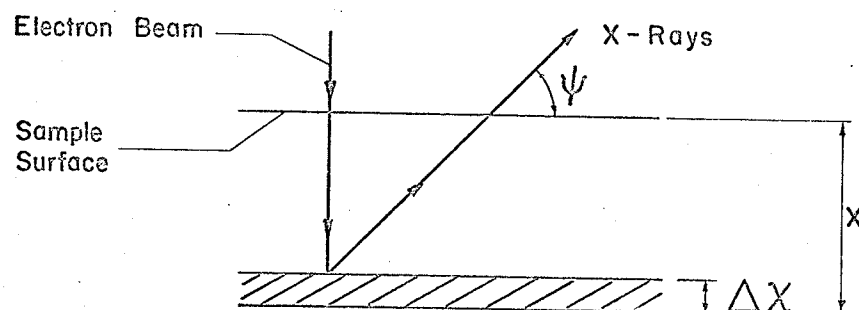
Electron-Probe Microanalysis

This instrument consists basically of an electron optics system for focussing a beam of electrons to a diameter of 0.1μ to 3μ on the specimen, and an x-ray optics system to analyze the emitted x-rays according to wavelength and intensity. In addition, an optical microscope system for viewing the specimen and selecting the exact area to be analyzed is incorporated in the instrument. In quantitative analysis the measured x-ray intensity (I_A) of a particular constituent of the specimen is related to composition. The L-series spectra are suitable for all atomic numbers fifty and larger and the K-series spectra are suitable for atomic numbers between fifty and eleven. In electron-probe analysis, as in x-ray fluorescence, the x-ray intensity from an element is not linearly related to composition (for a constant energy of the electron beam). Some of the factors responsible for non-linearity are enumerated below and will be briefly discussed in a non-mathematical fashion:

- 1) Matrix absorption of characteristic x-rays
- 2) Matrix enhancement of characteristic x-rays
- 3) Take-off angle (ψ) of x-rays
- 4) Atomic number and angle of incidence of electron beam
- 5) Surface condition of specimen.

1) X-radiation that passes through matter is always partly absorbed. Quantitatively the amount of absorption is given by μ , the mass absorption coefficient, which depends on the wavelength and the type of element. When electrons strike the sample characteristic x-ray spectra

of the elements present in the sample are produced in a layer ΔX cm thick and X cm below the surface as shown,



provided that the energy of the electrons is not below some critical value. " X " is usually 1μ to 3μ deep. It is clear that some x-rays will be absorbed as they emerge from the region in which they are produced and pass through the overlying matter. If an element whose abundance in a matrix is to be determined is in a matrix of high absorption the characteristic radiation of that element will be reduced more than if the element was in a matrix of low absorption, for the same angle " ψ " and the same electron beam energy. Clearly some correction, depending on the matrix element (Z) and the take-off angle " ψ " has to be applied. If " W_A " is the weight fraction of element "A" in a matrix of elements B, C, of weight fractions W_B , W_C respectively, then μ'_A the total mass absorption coefficient for wavelength λ_A , which is the characteristic x-radiation of element "A", is given by:

$$\mu'_A = W_A \mu_{AA} + W_B \mu_{BA} + W_C \mu_{CA} + \dots \quad \text{eq. (1)}$$

where μ_{AA} , μ_{BA} , μ_{CA} etc. are the mass absorption coefficients of the

elements "A, B, C" for the characteristic radiation of element "A" (λ_A).

In general if " I_A " is the total intensity of characteristic radiation of "A", it has been found that the function $F = \left(\frac{I_A}{W_A}\right) K$ where K is a constant which depends on μ' and ψ as $\mu' \csc \psi$. Tables of $\mu' \csc \psi$ vs. F for various electron beam energies have been constructed and are given by Birks (68). It follows that the intensity ratio for any two different compositions of a given element is given by: $\frac{I_1}{I_2} = \frac{F_1 W_1}{F_2 W_2}$ where the subscripts "1" and "2" refer to two different compositions of the same element in the same type of matrix. If the pure element is first used as a standard then the above equation reduces to $\frac{I_x}{I_{100\%}} = \frac{F_x W_x}{F_{100\%}}$ eq.(2) The ratio $\frac{I_x}{I_{100\%}}$ is determined experimentally, the ratio $F_x / F_{100\%}$ is calculated with the use of tables by iteration and W_x can then be calculated. To obtain "F" with the use of tables compiled as F vs. $\mu' \csc \psi$, " μ' " is calculated (eq. (1)), beginning with an estimate for " W_A, W_B, W_C " etc. and proceeding by re-iterating the complete calculation cycle sufficiently often until constancy in the calculated composition is obtained. Usually three or four reiterations are sufficient.

2) If the characteristic x-radiation of one of the components of the matrix "B, C,..." is sufficiently energetic to excite the characteristic radiation, radiation of the element "A" under study will be enhanced. It is known beforehand whether such a combination of elements is present in the specimen. An enhancement coefficient " K_F " is then applied to equation (2) i.e. $\frac{I_x}{I_{100\%}} = \frac{F_x}{F_{100\%}} W_A (1 + K_F)$ where

$$K_F = k E_{AB} W_B \left(\frac{\mu_{AB}}{\mu_B} \right) \left(\frac{V - V_{OB}}{V - V_{OA}} \right)^2$$
 k is an empirical constant equal to 0.6, the V_0 's are the respective voltage minima for characteristic x-ray excitation (available from tables), "V" is the operating voltage and E_{AB} , the excitation efficiency, again obtainable from tables. Since K_F depends on the W 's which are sought, an approximate K_F is first calculated based on reasonable choices of W 's, and by reiteration of the complete calculation cycle a final constant value of W_X and K_F is obtained. In the present investigation no enhancement corrections were necessary.

3) The path length of the emitted x-rays through the overlying matter is obviously dependent on the take-off angle " ψ " as can be seen from the simple diagram on page 31. Since "F" is dependent on " ψ ", the variation in intensity due to a variation in " ψ " has been incorporated into the tabular values of "F" and no additional correction is then necessary.

4) The "stopping power" an element has for electrons is a factor in determining the distance of penetration (X) of electrons into the specimen and thus partly determines the path length of the emitted x-rays through the sample matter. The "stopping power" among other things depends on Z/A where "Z" is the atomic number and "A" is the atomic weight. This ratio lies between 0.4 and 0.5 throughout most of the periodic table. "F" is a function of Z/A and the variation in "F" with atomic number is small. The greatest error will occur when the specimen contains two elements which are far apart in atomic number. Birks (68, Page 244) has compiled correction factors for atomic number (P_Z) by which the function $\mu' \csc \psi$ is multiplied

if such a correction is necessary. In the case of silver and indium the correction factor P_Z is quite small (0.955) since the two elements are only one atomic number apart.

The x-ray intensity is also a function of the angle of incidence of the electron beam and its energy. Since only relative intensities are determined i.e. $I_A/I_{100\%}$ and these factors are the same for both intensity measurements they are then instrumental constants which are known. When "F" is determined from tables one simply chooses the appropriate table for these constants.

5) The flatness of the specimen surface is important in electron probe analysis, more so than in x-ray fluorescence analysis. Since the x-rays come from the surface layer, surfaces that contain ridges and valleys cause variations in electron incidence and take-off angle giving rise to variations in observed x-ray intensity. The surface should be as flat as possible. Excessive polishing should be avoided since it tends to smear the surface layers giving erroneous composition analysis. For the same reason repeated etching should be avoided because components are removed selectively or in fact a new component may be deposited on the surface.

The determination of composition can now best be shown by an actual step by step sample calculation:

(All page references in the sample calculation refer to Birk's "Electron Probe Microanalysis" (68)).

Sample Calculation

Mass absorption coefficients:

Silver in Silver $\mu' = 475$ (page 215)

Silver in indium $\mu'' = 560$ (page 215)

Multiplier P_Z for Silver ($Z = 47$) is 0.955 (for 30KV)

$\psi = 15^\circ$ (instrumental constant)

Experimental:

- Intensity of silver (pure silver) $I'_{100\%Ag} = 4635$ cps
- Intensity of silver in a silver-indium sample $I'_X = 1505$ cps
- Background intensity = 23 cps in both cases
- corrected intensities $I_{100\%} = 4635 - 23 = 4612$ cps.
 $I_X = 1505 - 23 = 1482$ cps.
- Roughly estimated composition $\frac{1482}{4612} \approx 0.32$ or 32% Ag

Calculation leading to "F" values. For pure silver.

$$1) (P_Z) \mu' \csc 15^\circ = 0.955 \times 475 \times 3.86 = 1750 \text{ (from page 194 Table)}$$

$$F_{100\%} = 45.2$$

For 32% silver.

$$2) P_Z \mu' \csc 15^\circ = (0.955) \left[0.32 \times 475 + 0.68 \times 560 \right] (3.86) = 1960$$

$$F_X = 41.9 \text{ (Page 194)}$$

$$\frac{\text{Intensity in sample } (I_{0.32})}{\text{Intensity in pure Silver } (I_{1.00})} = \left(\frac{F_{0.32} W_X}{F_{1.00}} \right)$$

$$\frac{1482}{4612} = \left(\frac{41.9}{45.2} \right) W_X; \quad W_X = 0.347 \text{ silver.}$$

The weight fraction for silver (0.347) is then used in step 2) to obtain a new value for F_X and a new composition W_X is calculated. This process is repeated until W_X does not change.

X-Ray Diffraction Microanalysis

This technique consists of removing small particles of alloy from a microsection under a stereoscopic microscope with a hard and very sharp needle-point tool and analyzing the material by x-ray powder diffraction in the usual way.

With experience in manipulating the tool under the microscope individual phases in a heterogeneous alloy can be easily removed and analyzed, provided of course that the phase to be removed is not in the form of very small particles. Material from various areas of the same phase is scooped out or dislodged repeatedly and carefully transferred to a glass slide with the needle-point tool until sufficient material is collected for x-ray analysis. A small amount of nail polish serves as a binder to work all the sample material into a tiny ball under the microscope. During this operation the plasticity of the binder is controlled with a paper tissue corner dipped into acetone and brought into close proximity to the sample. The free end of a thin glass fibre which is mounted in the camera sample holder is dipped into nail polish and brought into contact under the microscope with the hardened sample ball. When the small sample is firmly attached to the tip of the glass fibre it is aligned in the powder diffraction camera in the usual way. It is essential that a stereoscopic microscope be used for the whole procedure and not an ordinary microscope which reverses the image, otherwise manipulation under the microscope becomes hopelessly difficult and uncoordinated.

This method of obtaining sample material for analysis by x-ray diffraction has two obvious advantages over the usual method of filing or grinding a bulk sample. Firstly, individual phases in a heterogeneous sample can be analyzed under favourable conditions, and secondly the sample is less deformed than when powder or when filings are produced. If the phase is brittle tiny blocks of single phase or single grains can be dislodged with little deformation of these grains. This method might be used to advantage in obtaining small single crystals from a multi-grained single phase when it would be otherwise difficult to obtain single crystals of this material.

Photomicrography

This is a very important technique in the study of alloys and metals, which involves the observation, under the microscope, of the gross structural details of the metal or alloy. The most important part of metallography is the preparation of the specimen. In general, the procedure of specimen preparation consists of six stages:

1. Sectioning
2. Coarse grinding
3. Mounting
4. Fine grinding
5. Rough polishing
6. Final polishing.

The first two stages need hardly any comment except to say that precautions must be taken to prevent shattering and "plucking" of the specimen and to minimize heating of the specimen so as not to obviate the efforts of annealing. The specimen is usually mounted in 1" to $1\frac{1}{2}$ " circular blocks of plastic material in a hot press to facilitate handling during subsequent fine grinding and polishing.

The purpose of fine grinding is to remove and limit, by proper selection and sequencing of abrasives, the zone of deformation caused by "sectioning and "coarse grinding" of the specimen, prior to mounting. As this layer of gross deformation is being removed a new layer of lesser deformation will be forming, caused by the action of the "fine grinding"

abrasive grains. This deformation will not be as severe and therefore not as deep as the first and will subsequently be diminished by application of a finer abrasive. "Fine grinding" continues using progressively finer abrasives until the deformation is shallow enough to be effectively removed by "rough-polishing".

The abrasive materials and sizes most often used for "fine grinding" are silicon carbide and diamond paste of 100 to 25 microns and 15 to 1 microns respectively. The final polishing stage should remove the last traces of the deformed layer and reveal the true microstructure of the specimen.

A wide range of abrasives is available for "final polishing". Gamma aluminum oxide, magnesium oxide and chromium oxide are probably the most commonly used materials. Magnesium oxide is particularly suitable for aluminium based alloys. Diamond pastes of $\frac{1}{4}$ to 0.05 microns are also available and are used in special cases. The choice of abrasive and the type of cloth used for fine grinding and rough polishing are important, but will depend on the properties of the alloy being prepared. No rules for this can be given, and success is a matter of experience.

Following the final polishing stage etching may be applied followed by repolishing to reveal the microstructure more clearly. Although compilations of various etching reagents suitable for particular alloys exist (34), the choice of the proper etching reagent is a matter of some trial and error and experience.

PREVIOUS RELEVANT INVESTIGATIONS

The Pure Metals

Silver crystallizes with a face-centred cubic lattice with cell edge $4.086\text{\AA}$ (16). The interatomic distance in the lattice is $2.888\text{\AA}$ (16). The melting point of pure silver is 960.8°C (16). Silver is not attacked by oxygen, but liquid silver dissolves oxygen, about twenty times the volume of the metal at the melting point (17). All oxygen is rejected on solidification. The atomic radius of silver is $1.444\text{\AA}$. The electronegativity of silver is 1.8 (2).

Indium crystallizes with a face-centred tetragonal lattice with cell edges $a = 4.594\text{\AA}$, $c = 4.951\text{\AA}$ (16). The interatomic distance is $3.25\text{\AA}$. The crystal structure is also described as "cubic close packed with some distortion" (62). The melting point of indium is 156.2°C (16). Cold air has no action on indium but, when hot, indium is oxidized by air to In_2O_3 . Nitrogen and hydrogen do not react with indium up to 900°C (18). No allotropic forms of indium are known. The atomic radius of indium is $1.625\text{\AA}$. The electronegativity of indium is 1.8 (2).

Aluminium crystallizes with a face-centred cubic lattice with cell edge $4.0491\text{\AA}$ (16). The melting point of aluminium is 660.2°C (16). It is well known that aluminium reacts with oxygen to form Al_2O_3 even at room temperature. The rate of oxidation is low however. Aluminium absorbs hydrogen at high temperatures (e.g. 1.87 cc. at $900^{\circ}\text{C}/100\text{ gm. Al}$ (19)). When heated it reacts with nitrogen to form Al N . Above 1000°C

it reacts with carbon to form Al_4C_3 (19). The atomic radius of aluminium is $1.431\text{\AA}$. The electronegativity of aluminium is 1.5 (2).

The Binary System Aluminium-Indium

This binary system was first investigated by S. Valentiner and I. Puzicha (60) by means of thermal analysis, photomicrography and x-ray powder diffraction. They found the two metals to be largely immiscible in both the solid and liquid states. The limits of miscibility in the molten state at 634°C were given as 13 and 98 wt. per cent indium respectively. Aside from these two experimental points no further investigation of the miscibility as a function of temperature was made, but two phase-reactions, a monotectic and a eutectic, were reported by these authors at 634°C and 156°C respectively.

E. Raub and M. Engel (48) who also investigated this system found the mutual solubility to be 17.3 and "90 or more" per cent indium respectively at 634°C . In other respects the two investigations agreed. A.N. Campbell et al (20) reinvestigated the system employing quenching and chemical analysis. The results differed somewhat from those of the previous investigations. In particular, they found the indium-rich liquidus and the isothermal reactions to be at a somewhat higher temperature. At 638.6°C they found the mutual solubility to be 20.5 and 97.2 per cent indium respectively.

J. M. Kuzmak (41) attempted to determine the "miscibility gap" but due to experimental difficulties did not wholly succeed.

A.N. Campbell and R. Wagemann (72) determined the boundaries of

mutual solubility completely in the molten state as a function of temperature. The critical temperature and composition were reported as 945°C and 68.8% indium respectively. The binary system Aluminium-Indium which is shown in Fig. 4, may thus be considered to be completed.

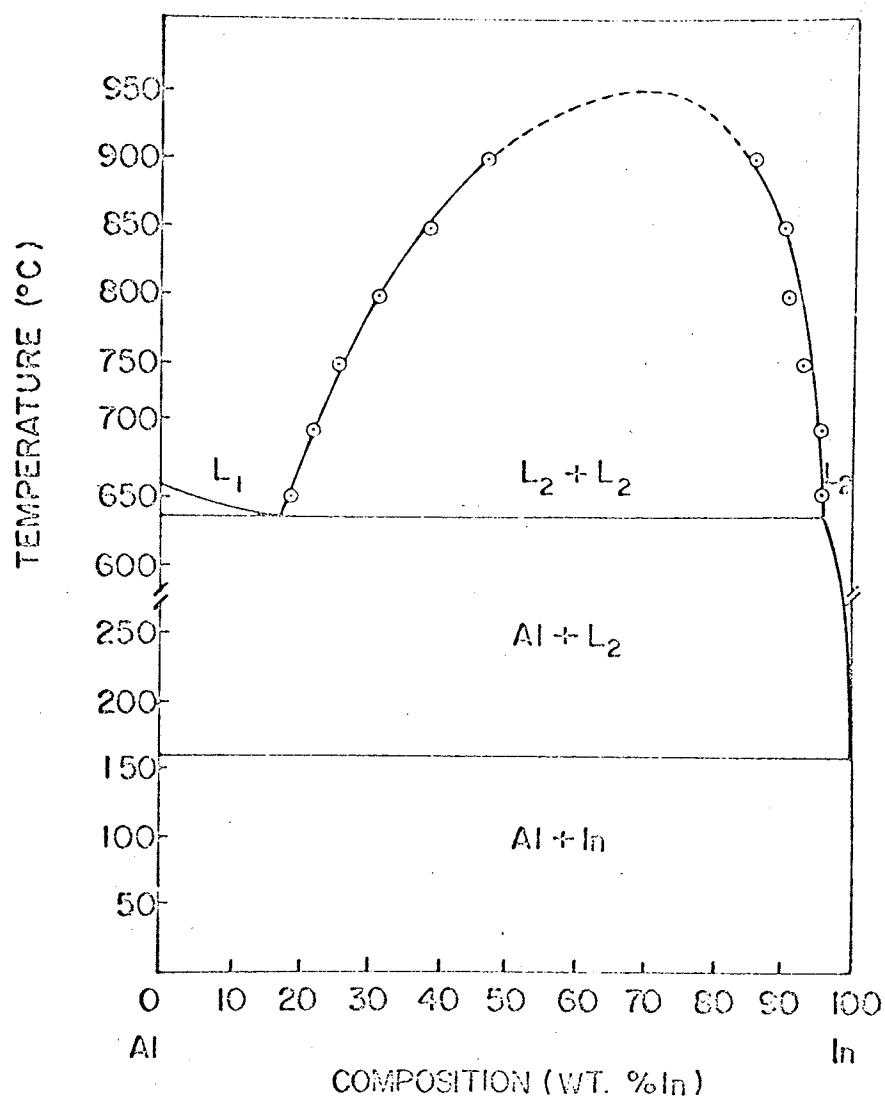


Fig. 4. The System Al-In (from Hansen (79), supplemented by data of Campbell and Wagemann, (72)).

The Binary System Aluminium-Silver

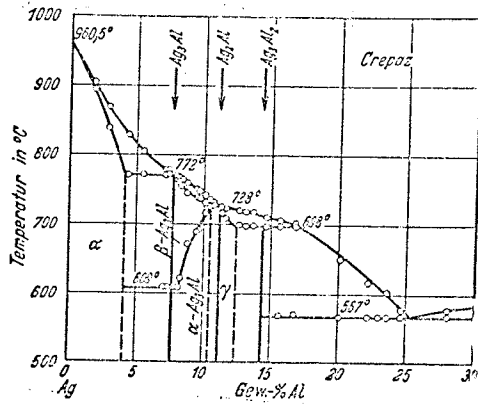
Extensive work by many investigators has been done to establish the currently accepted phase diagram of this system shown in Fig. 6. The four smaller phase diagrams shown in Fig. 5, which were put forward by various people at various times convey graphically something of the evolutionary process that studies on the system have undergone.

C.R.A. Wright (69) showed that the two metals are completely miscible in the liquid state.

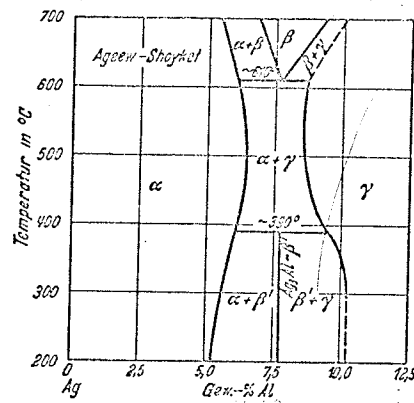
H. Gautier (22) was the first to investigate the liquidus. He found a maximum in the liquidus at 11.11 per cent aluminium corresponding to Ag_2Al .

The complete phase-diagram was first established by G.I. Petrenko (46) by thermal analysis and photomicrography. He believed that distinct compounds Ag_2Al (11.11% Al) and Ag_3Al (7.69% Al) existed but he did not obtain a maximum in the liquidus curve as was found by H. Gautier (22).

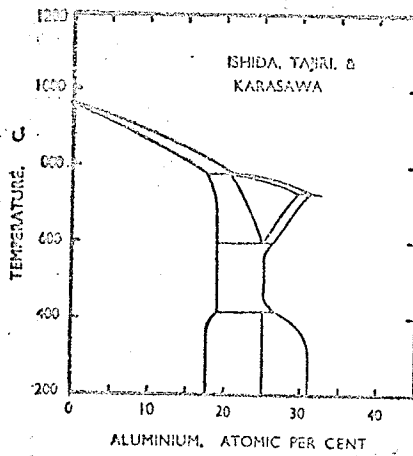
A. Westgren and A.J. Bradley (63), employing x-ray diffraction, found a homogenous phase corresponding in composition to $\text{Ag}_3\text{Al}(8')$ which existed over a very narrow composition range and had a β -manganese type structure with twenty atoms per unit cell. In addition they found a second intermediate phase (γ) with a hexagonal close-packed crystal structure and a homogeneity range of 8.5 - 14.5 per cent aluminium at no specified temperature. They also investigated the α -solid-solubility limit giving it as 19 atomic per cent, again without specifying the corresponding temperature. The above authors rejected the existence of the compounds Ag_2Al



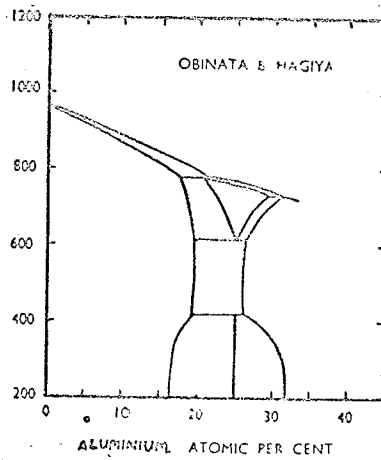
By E. Crepaz (38)



By N. Ageew & D. Shoyket (43)



By Ishida, Tajiri and
Karasawa (36)



By Obinata & Hagiya (45)

Fig. 5. The System Ag-Al at Various Times.

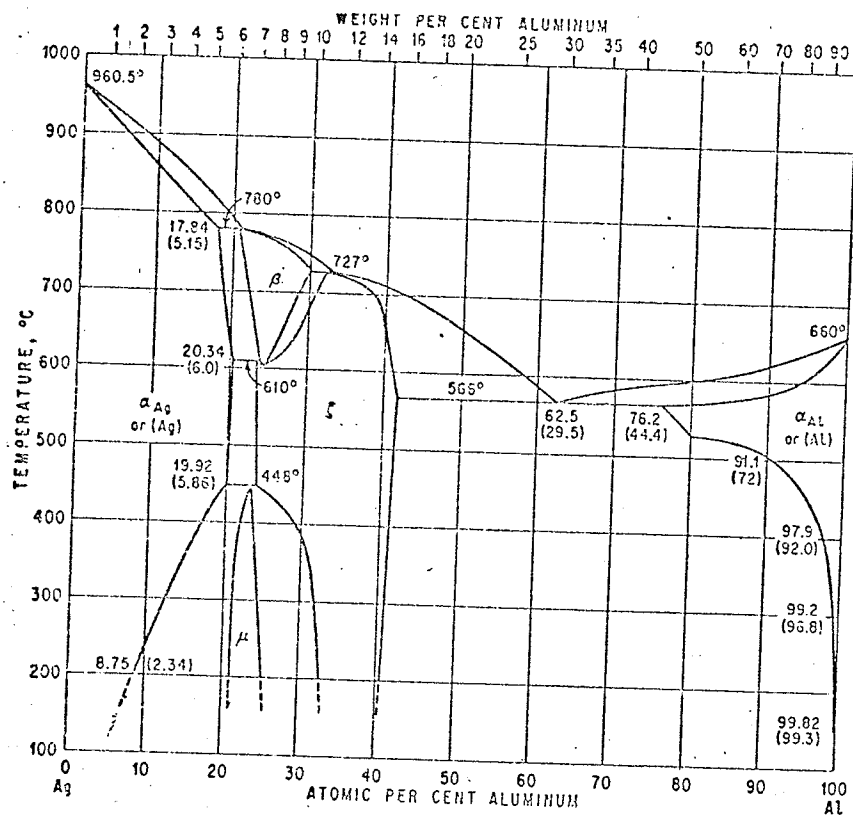


Fig. 6. The System Ag-Al

(from Hansen, 79).

and Ag_3Al_2 which were reported by W. Broniewsky (23) on the basis of resistance and temperature-coefficient of resistance measurements. The " β " and " γ " phases were later designated by W. Hume-Rothery et al (33) as " μ " and " ζ " respectively.

Although nearly all investigators seemed to agree that a high-temperature β -phase existed, there was disagreement regarding the transformation of the β -phase. According to G.I. Petrenko (46) and A. Westgren and A.J. Bradley (63), β transforms into β' at approximately 610°C . The findings of W. Hofmann and K.E. Volk (32) indicated that the high-temperature β -phase had a cubic bodycentred crystal lattice above 605°C , transforming into an hexagonal close-packed phase at some temperature between 605°C and 570°C (and not into β'). N. Ageew and D. Shoyket (42,43,44) found the β -phase to break up into a mixture of two phases ($\alpha + \gamma$) at 610°C , while at slightly below 400°C the two phases supposedly recombine to form a single phase (β'). F.E. Tishchenko (56,57) found that the β -phase (which he calls Ag_3Al) transforms into β' at 606°C . He also reported the compound Ag_3Al_2 having a melting point of 752°C and becoming stable only above 711°C . Below this temperature it supposedly decomposes into solid solution of aluminium in Ag_2Al . According to M. Hansen (26) the conclusions of Tishchenko are erroneous with regard to the compound Ag_3Al_2 .

The partial phase-diagrams of E. Crepaz (35,38) N. Ageew and D. Shoyket (42,43,44) S. Ishida, H. Tajiri and M. Karasawa (36) and I. Obinata and M. Hagiya (45) given in Fig. 5 reflect the diverse results of investigations on this binary system at that time. T.P. Hoar and R.K. Rowntree clarified some of the controversy (31).

Two peritectic reactions occur in this system which had variously been determined by different workers: for $\alpha + L \rightleftharpoons \beta$ as 770°C (63); 779°C (31); 770°C (46); 779.8°C (33); 771°C (57,58); for $\beta \rightleftharpoons L + \gamma$ (at 10.0 - 10.8% Al), $718 - 723^{\circ}\text{C}$ (63); 729°C (31); 722°C (57,58); 718°C (46); 726.9°C (33). According to E. Crepaz (38) a third peritectic reaction takes place at 698°C due to decomposition of Ag_3Al_2 . Similarly the eutectic temperature and composition were variously determined as 567°C (46); 558°C (27); 568°C (38); 566°C (49); at 30% Al (27,46); 38.0% Al (28); 35% Al (35); and 25.5% Al (38).

The silver α -solid solution boundary was first determined by G.I. Petrenko (46) and redetermined by A. Westgren and A.J. Bradley (63), W. Broniewsky (23) B. Beckmann (25), M. Hansen and G. Sachs (27) and W. Humelothery, G.W. Mabbott and K.M.C. Evans (6), with results which agreed fairly well. By means of density and lattice parameter measurements A. Westgren and A.J. Bradley (63), C.S. Barrett (80), E. Jette and F. Foote (37) and S. Kukubo (40) claimed that the α -solid solution is of the substitutional type but R.T. Phelps and W.P. Davey (47) disagreed with this conclusion.

The aluminium σ -solid solution (α Al) boundary was determined by M. Hansen (27,28). Apparently no such σ -phase was found previously by G.I. Petrenko (46) but W. Broniewsky (23) did find such a terminal phase. W. Kroll (39) and M. Tazaki (55) later confirmed M. Hansen's (27,28) work.

G.V. Raynor and D.W. Wakeman (49) later redetermined the solid-phase boundaries. In contrast to reports of previous workers they found that the σ -boundary was not smooth, but exhibited a marked change in direction in the region of 49.4 per cent Ag (by weight) at a temperature of 526°C. The maximum solid solubility was reported as 55.6 per cent Ag (by weight) at the eutectic temperature of 566°C.

W. Hume-Rothery, G.V. Raynor, P.W. Reynolds and H.K. Packer (33) confirmed the existence of a high-temperature β -phase, established the boundaries and redetermined the crystal structure, viz. cubic body-centred, and found the transformation temperature $\beta \rightarrow \gamma (\zeta)$ to be 603°C. They confirmed the structure of the γ -phase (ζ) as hexagonal close-packed. They also confirmed the structure of the β' -phase (μ) to be of the β -manganese type, and established that it existed at 7.7 per cent aluminium (by weight or 25 atomic % Al) within a narrow range of composition. The binary phase diagram of the system Aluminium-Silver given in Fig. 6 embodies the work and results of many people. The aluminium-rich side is mainly due to M. Hansen (27,28) while the silver-rich side, in its finer details, is due to W. Hume-Rothery and associates (33).

A voluminous body of literature also exists on the important non-equilibrium aspects of this system, such as precipitation, kinetics, supersaturation and metastable phases, but will not be reviewed here since they do not represent equilibrium states.

The Binary System Silver-Indium

V.M. Goldschmidt (24) found an hexagonal close-packed phase (Ag_3In) (δ or γ') having lattice constants $a = 2.950 \text{ kX}$ $c = 4.769 \text{ kX}$.

L.L. Frevel and E. Ott (21) found three intermediate phases at room temperature (in addition to the two terminal solid solutions) two of which they reported to be hexagonal and the third to be face-centred cubic, "very rich in indium". The latter phase is presumably the indium-rich face-centred tetragonal phase " ϕ ". Only one hexagonal phase is known to exist in this system.

The first to investigate the system completely and systematically by means of x-ray powder diffraction, photomicrography and thermal analysis were Von F. Weibke and H. Eggers (61). They established the liquidus, the various reaction isotherms and some approximate phase boundaries. Their phase-diagram is shown in Fig. 1. Briefly, some of their results are: The silver-rich terminal solid solution extends to 19.4 per cent indium (by wt.) at room temperature and 19.8 per cent indium at 693°C . A phase " δ " exists within the composition range of 26.8 - 33.1 per cent indium (by wt.) at room temperature. Neither Ag_3In (26.2% In) nor Ag_2In (34.7% In) fall within the homogeneous range of the δ -phase. On the indium-rich side a phase (ϕ) exists with a few tenths of a percent range in composition at either 70 or 75 per cent indium (by wt.). They apparently were unable to establish what the composition of that phase was more closely, because of conflicting experimental data. They also point out that no difference in x-ray powder diffraction patterns could be observed for the " γ " and " δ " phases. The latter symbol was simply introduced to account for certain

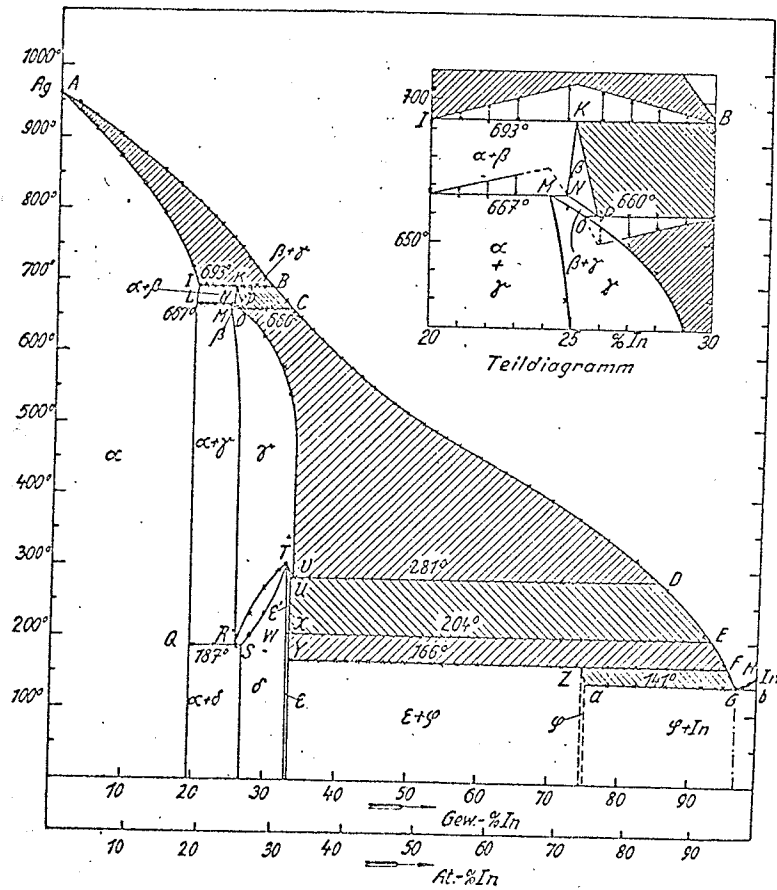


Fig. 1, repeated from page 3.

The System Ag-In by Weibke and Eggers (61)

observed thermal effects. They did not attempt to determine the crystal structures of the intermediate phases.

W. Hume-Rothery et al. (6) investigated the silver-rich region of the system only, with the primary aim of establishing more precisely the solubility limit of indium in silver, as a function of temperature. The liquidus and α -solidus as determined by these authors agree well with those determined by Von F. Weibke and H. Eggers (61), but they differ in the position of the α -phase boundary by approximately one per cent. W. Hume-Rothery et al. (6) also carried out high-temperature x-ray diffraction investigations establishing that the β -phase, which is stable only in the temperature range of 660° to 693°C , is bodycentred cubic. In this respect their investigation appears to have been confined to the $(\alpha + \beta)$ region and no lattice parameters for the β -phase were reported.

D.P. Morris and I. Williams (67) determined the lattice parameter of the β -phase by high-temperature x-ray diffraction as $3.3682\text{\AA}$ at 684°C .

Von E. Hellner (29,30) Fig. 2, who investigated this system with the aim of determining the crystal structure and the extent of the regions of homogeneity of the intermediate phases found that an alloy of 26.6 per cent indium (by wt.), corresponding to Ag_3In , was homogeneous at both 600°C and 150°C with no basic difference in crystal structure occurring at these temperatures. He assumed that a single phase would also be observed at room temperature at this composition. He found that the "single-phase" region " δ " reported by Von F. Weibke and H. Eggers (61) did not exist and was really a heterogeneous region consisting of $(\gamma' + \epsilon')$ phases. He reported that

the γ' -phase had a composition range Ag_3In to Ag_2In (Ag_3In falling within the homogeneous region) and that it had a hexagonal close-packed structure with $a = 2.948 \text{ \AA}$ and $c = 4.794 \text{ \AA}$, in good agreement with the values reported by V.M. Goldschmidt (24). He found the ϵ' -phase had a composition corresponding to Ag_2In (34.7% In by wt.) and that it had a γ -brass type crystal structure (complex cubic) with $a = 9.885 \text{ \AA}$ but apparently no composition range was determined. The composition of the ϕ -phase he reports as AgIn_2 , having a face-centred tetragonal structure of the type CuAl_2 , with lattice constants $a = 6.869 \text{ \AA}$ and $c = 5.604 \text{ \AA}$. The limits of composition range were not determined. The Miller indices for the ϵ' and ϕ phases of the x-ray diffraction lines are given (29) but not for the γ' phase.

To explain some heat effects observed at 204°C but with no corresponding change being observed in the x-ray diffraction patterns Von F. Weibke and H. Eggers (61) postulated an order-disorder transformation $\epsilon' \rightleftharpoons \epsilon$ which Hellner (29) retained without having any experimental proof for doing so. A similar situation exists with regard to the $\gamma' \rightleftharpoons \gamma$ order-disorder transformation postulated by Hellner (29) to explain heat effects observed by Von F. Weibke and H. Eggers (61) at 187°C . The modified phase-diagram of Von E. Hellner is shown in Fig. 2. The α -phase boundary of this system was also very carefully determined by E.A. Owen and E.W. Roberts (51) over the entire temperature range, and the results are in very good agreement with those of W. Hume-Rothery et al. (6) and Weibke and Eggers (61) so that this part of the system can be considered to be well established, but, in the composition range of 23 to 40 per cent indium, the data of the two previous investigations (29,61) are in conflict in a number of instances, which only further work can clarify.

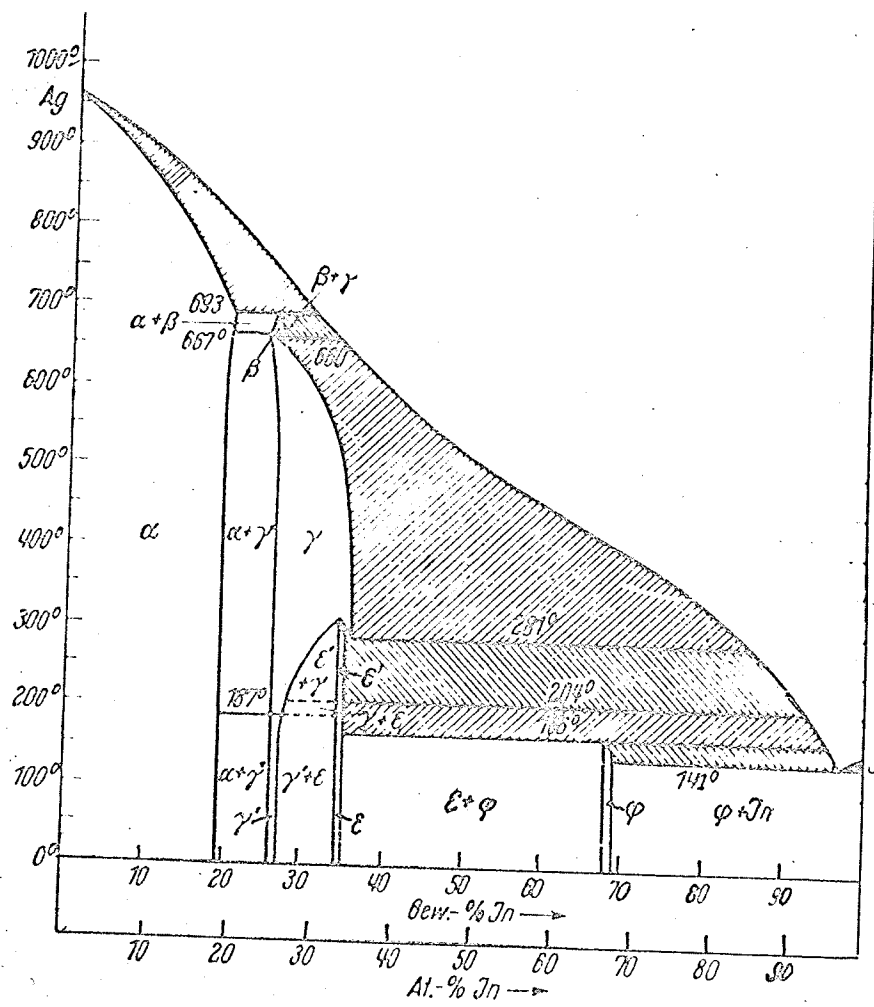


Fig. 2, repeated from Page 4.

The System Ag-In by Hellner (30)

The Ternary System

The region of immiscibility of the molten metals in the ternary system was determined as a function of temperature and composition by Campbell and Wagemann (72). The liquidus was also completely determined (71). These are the only investigations carried out on the ternary system.

EXPERIMENTAL TECHNIQUES

Purity of Metals

Silver: obtained from Matheson Coleman and Bell Co. Ltd., was in needle form and stated to be 99.999% pure.

Indium: Ingot form, 99.99 per cent indium or better, obtained from the Consolidated Mining and Smelting Company of Canada Ltd.

Aluminium: Ingot form, 99.994 per cent aluminium, (0.0019% Fe; 0.0018% Si; 0.0018% Cu), obtained from The Department of Mines and Technical Surveys, Mines Branch, Ottawa.

The certificates of analysis were supplied by the respective companies and the government agency.

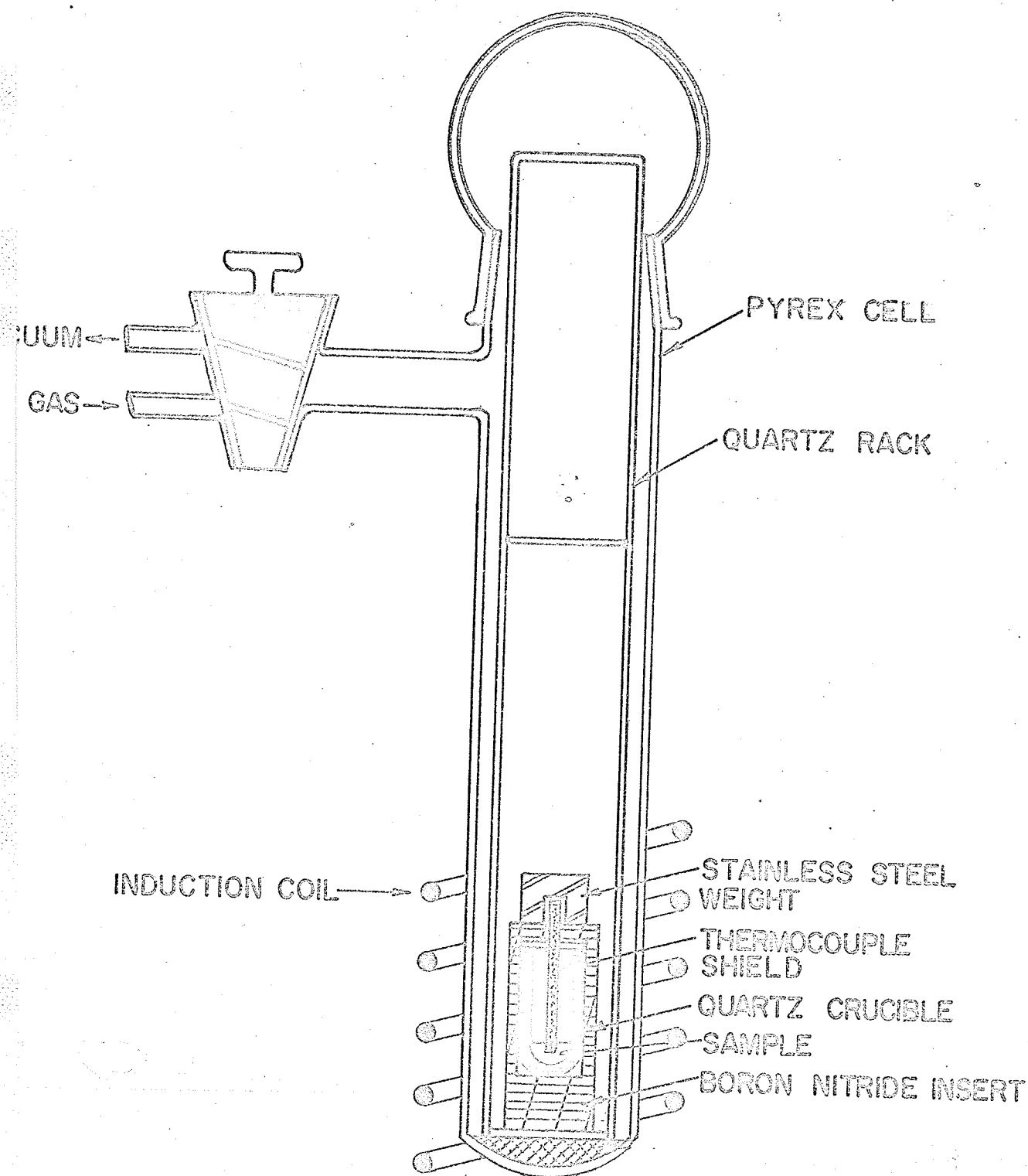


Fig. 7 Homogenization Cell

Preparation of Alloys

Alloys of the desired composition were prepared by weighing accurately the pure components in the required proportions. Prior to any heat treatment or differential thermal analysis all alloys were homogenized in an electrical induction furnace under inert atmosphere in a "cell" shown in Fig. 7. Silver-indium alloys were contained in a quartz thimble (tube) within a boron nitride cylinder; quartz has no action on silver or indium under the condition in question. In the molten state the alloy was stirred vigorously by induced currents - the stirring action could be observed visually quite clearly when the supporting container (boron nitride cylinder) was not covered. After five to ten minutes of stirring in this fashion the alloy was allowed to cool, after which it was subjected to heat treatment or differential thermal analysis. In the latter case the boron nitride cylinder containing the alloy was inserted inside the copper cylinder and transferred to the differential thermal analysis "cell" Fig. 10. Subsequent alloys of different composition which were to be analyzed by this method were prepared by successive additions of pure components of the exact amount to this original alloy which was then homogenized as described, after each addition. After eight different alloys were prepared by successive additions and analyzed thermally a totally new alloy was prepared. Ternary alloys were treated in the same way, except that small aluminum crucibles were used rather than quartz, because aluminium is known to attack quartz. The temperature of homogenization was approximately 1000°C . A faint metallic deposit was observed on the glass walls in the cold region of

the "cell" due to volatilization, but even after ten repeated homogenization trials it was evident that the quantity of metal volatilized was very small in relation to the weight of the sample which was in the order of ten grams. Chemical analysis for silver was performed on two separate alloys which were subjected to ten homogenization and differential thermal analysis cycles, and the loss due to volatilization was confirmed to be negligible. The compositions quoted are based on weighed-in amounts of components. All compositions are given in terms of weight per cent unless otherwise stated.

Alloys to be used for x-ray diffraction analysis and photomicrography were homogenized as described but no thermocouple shield was frozen into the alloy. After cooling, the alloy was cut into three or four pieces which were sealed individually into evacuated quartz ampules and then subjected to the desired annealing treatment which is compiled in Table 1, for the binary alloys.

The preparation of microsections consisted of grinding the annealed specimen with successively finer abrasives of silicon carbide using water as a lubricant. Diamond paste of 15μ , 8μ and 1μ respectively was used successively in the fine-grinding stage. The specimens were finally polished very briefly with chromic oxide using a weak detergent solution, as a lubricant. Considerable difficulty was encountered in trying to obtain scratch-free surfaces of heterogeneous alloys due to the large difference in hardness of the micro-constituents of such alloys, which consisted of hard and brittle intermetallic phases embedded in a very soft matrix of nearly

pure indium. Similar difficulties were encountered in etching these alloys. The soft matrix was readily attacked by all etching reagents tried, while the intermetallic phases showed great chemical resistance to most such reagents when immersed for ten to fifteen seconds. The most suitable etching reagent for heterogeneous alloys of indium-silver was an ammonium persulfate solution (34, page 114) which had the peculiar quality of colouring the δ -phase brown whenever it was present, and thus could be used conveniently to identify this phase unambiguously under the microscope. Alloys which did not contain the soft indium matrix were dip-etched in nitric acid.

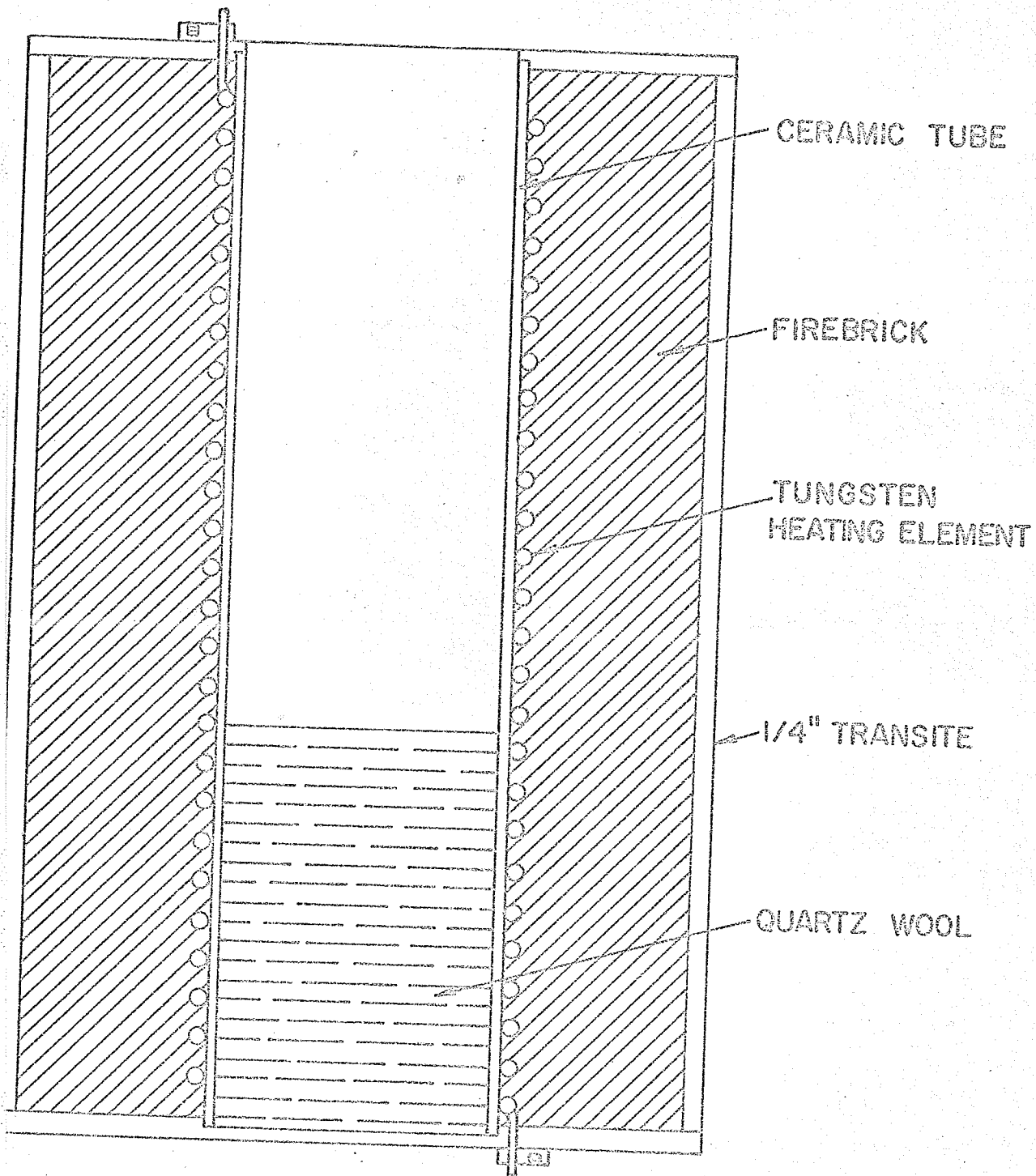


Fig. 8. Furnace

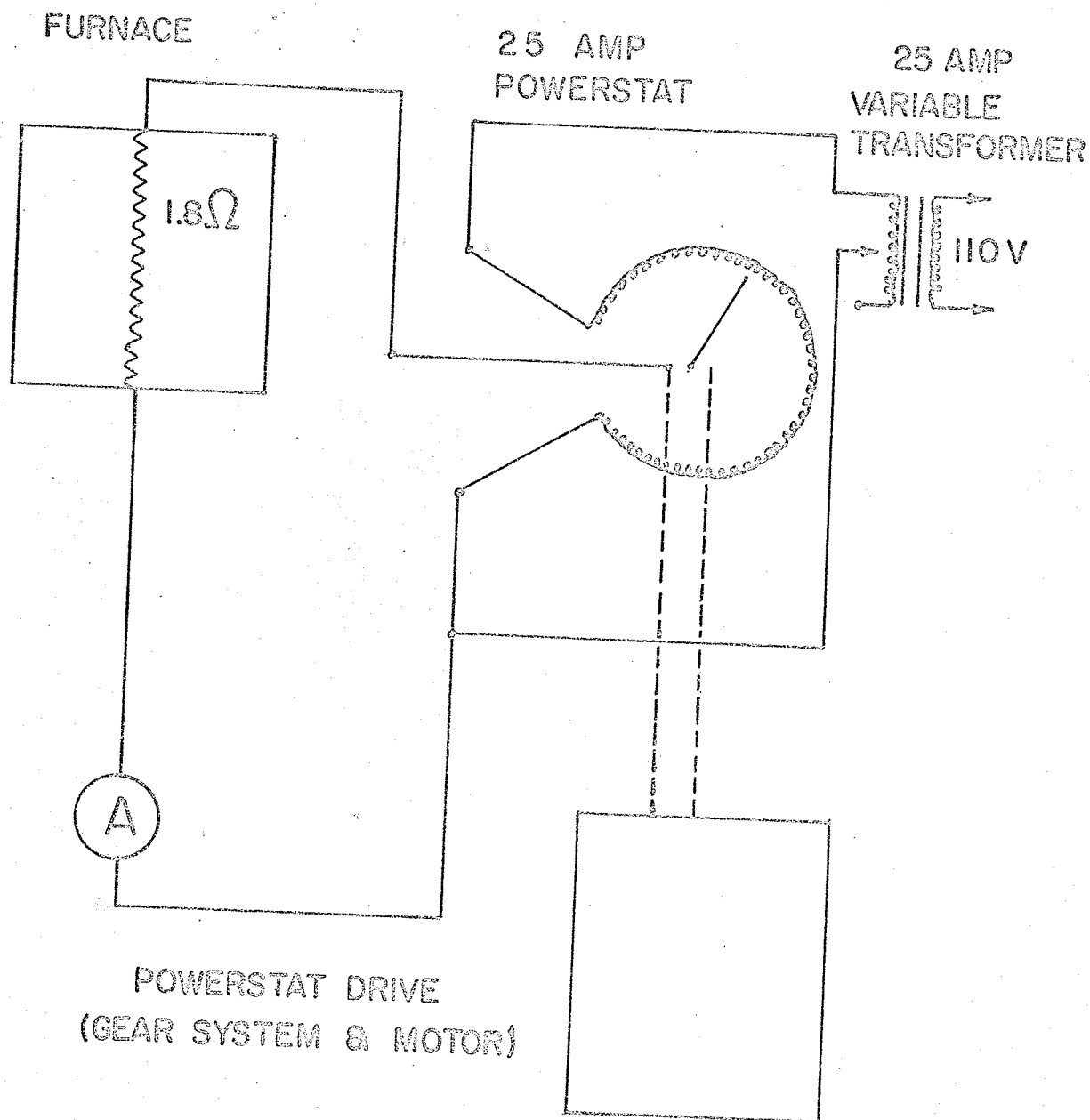


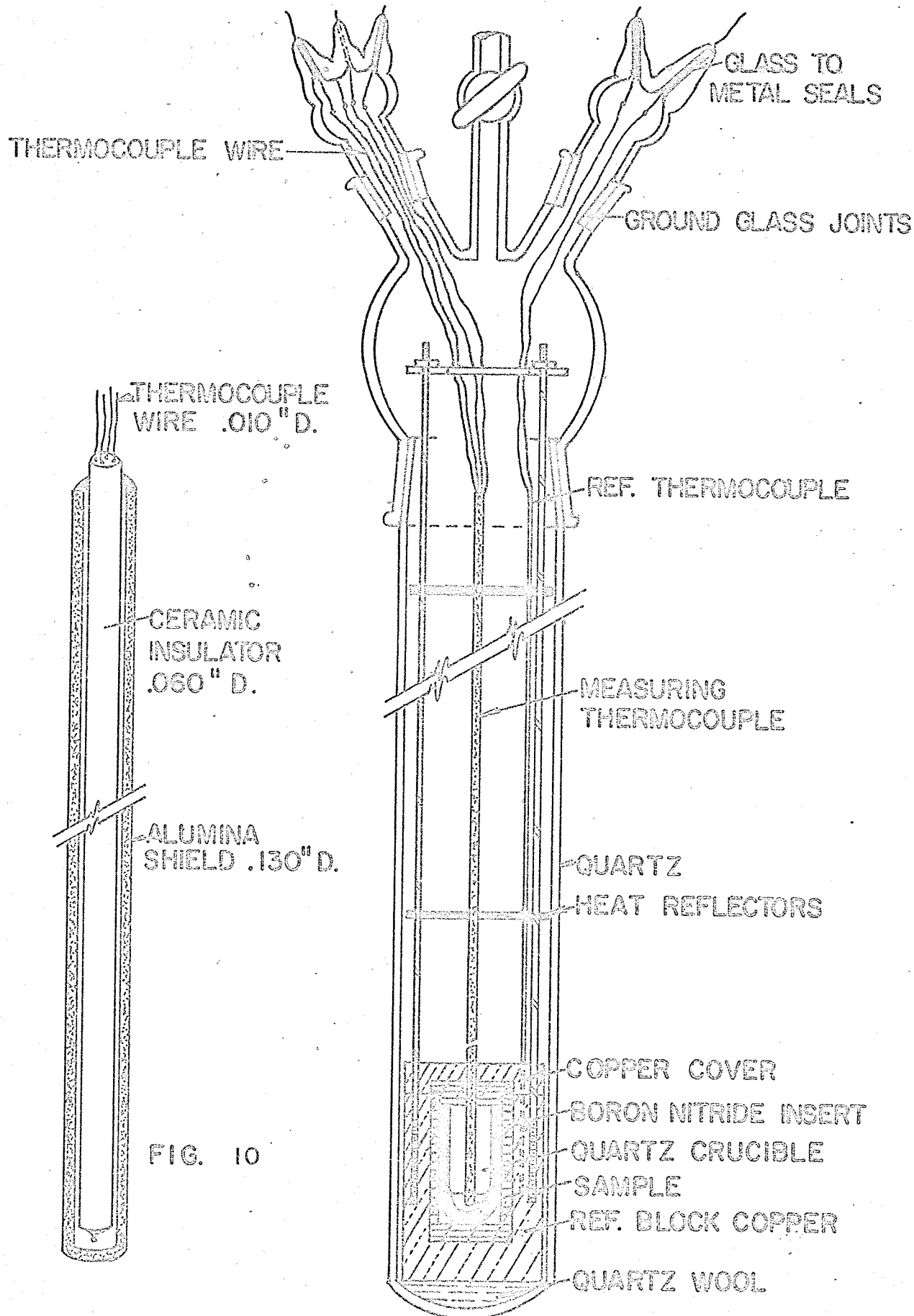
Fig. 9. Schematic arrangement of differential thermal analysis apparatus.

Differential Thermal Analysis

A "Hoskins" resistance-type furnace (1.8Ω) was used to heat the alloys. It consisted essentially of a vertical tube of a refractory material, fifteen inches high, $1\frac{3}{4}$ inches internal diameter, closed at the bottom and packed inside with quartz wool to a height of five inches. The whole cylindrical tube upon which the heating element was wound was well insulated thermally (Fig. 8). Current was drawn from a low-voltage variable ("Surges") transformer. The output from this transformer was connected to a 25 amperes variable auto-transformer ("powerstat") which was mechanically coupled via a gear-reduction system to an electric motor. The "powerstat" was protected by end-switches, switching off the driving motor when the maximum or minimum positions were reached. The drive was reversible, allowing for controlled heating and cooling. The variation of temperature rate was from 0.8°C to 0.5°C per minute giving very nearly a linear variation of temperature with time. A schematic diagram of the simple heating circuit is shown in Fig. 9.

The differential thermal analysis "cell" (D.T.A. cell, Fig. 10) consisted of a large quartz tube containing a copper cylinder and the sample. The "cell" could be evacuated or filled with inert gas by means of an auxiliary filling and evacuation system. Electrical connections with the thermocouples in the "cell" were made via vacuum-tight glass-to-metal seals in the top of the "cell". The copper cylinder which served as an inert reference body contained a smaller boron nitride cylinder which in turn contained the small quartz or alundum thimble with the sample. Both cylinders had tight-

DIFFERENTIAL THERMAL ANALYSIS CELL



fitting covers with small coaxial holes in the center through which the alumina thermocouple tube could be inserted. The reference thermocouple was situated in the wall of the copper cylinder parallel to the sample thermocouple. The boron nitride cylinder served to isolate physically the alloy from the copper cylinder preventing contamination through the vapour phase. In addition it isolated the alloy thermally, retarding somewhat the rapid heat exchange between the sample and the reference body. The "D.T.A. cell" fitted vertically into the tubular furnace. Fig. 10 shows the "D.T.A. cell".

The vacuum and purification system consisted of a mechanical vacuum pump and a mercury diffusion pump arranged in the usual manner, a small "copper-copper oxide" furnace and cold traps. Prior to analysis the "D.T.A. cell" was evacuated, filled with helium gas, evacuated again and finally filled with purified helium which had been allowed to pass slowly through the "copper furnace" to remove traces of oxygen which were present in the commercially available helium. The water vapour was removed from the gas in the cold traps at liquid nitrogen temperature.

The sample temperature and difference in temperature were measured with chromel-alumel thermocouples and a "Honeywell Electronic 15" two-pen multirange recorder (Fig. 11). All external cables in the temperature measuring circuit were metal shielded to minimize interference from stray potentials. The cold-junction of the thermocouple was maintained at $30.0^{\circ}\text{C} \pm 0.1^{\circ}\text{C}$. The calibration of the thermocouple was made in terms of millivolts on the "recorder" at the temperature of freezing of pure metals versus the accurately-

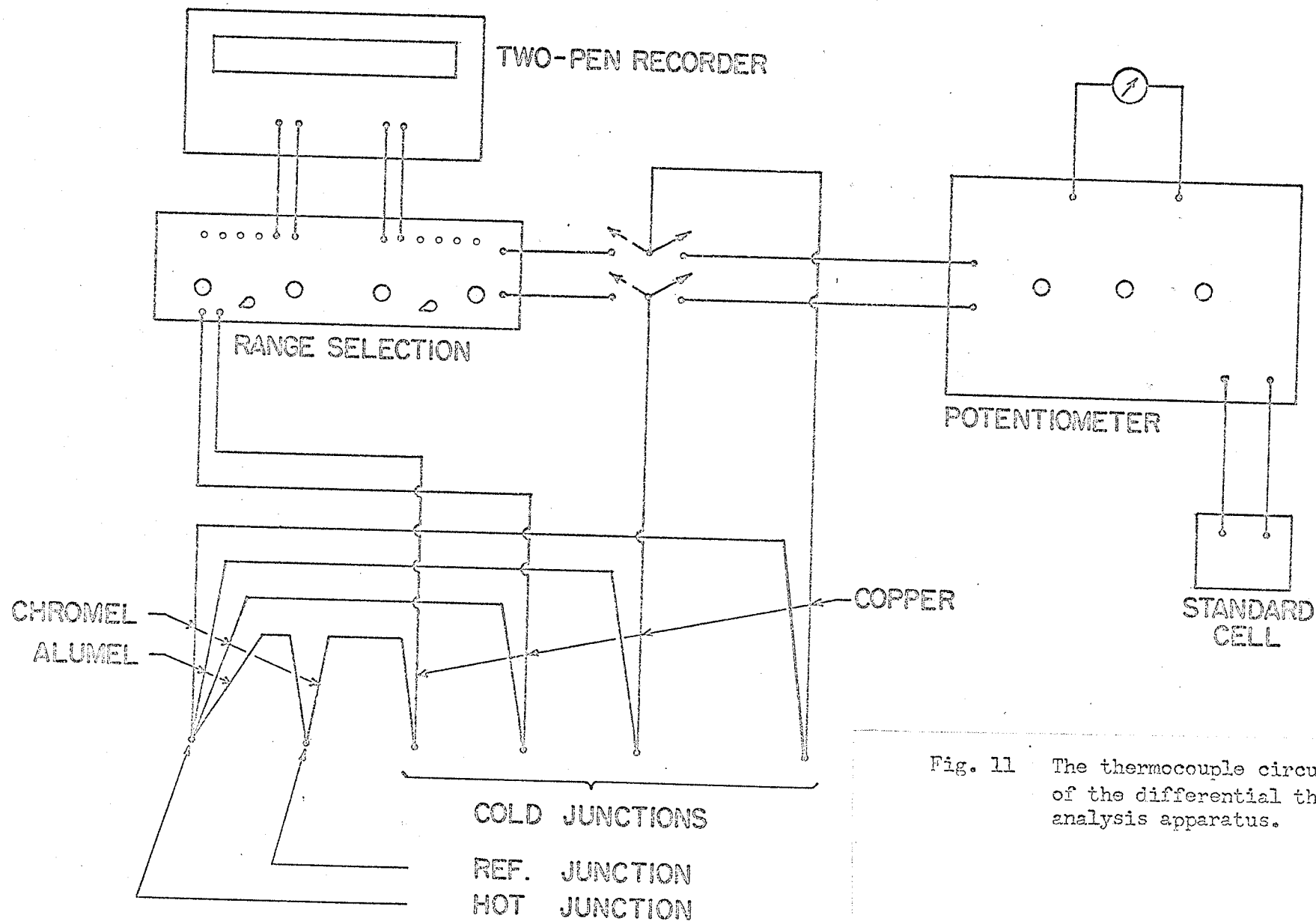


Fig. 11 The thermocouple circuit of the differential thermal analysis apparatus.

known freezing points of the following metals: silver, aluminium, zinc cadmium, tin and indium, (16), all of 99.99 per cent purity or better.

The principal errors in temperature were estimated to be $\pm 1.0^{\circ}\text{C}$ due to an uncertainty in measuring potential, and $\pm 0.5^{\circ}\text{C}$ due to an uncertainty in reading the calibration graph giving a total estimated error in temperature of $\pm 1.5^{\circ}\text{C}$ over the entire temperature range of room temperature to 700°C .

A schematic drawing of the "D.T.A." circuit and components is shown in Fig.11.

X-Ray Powder Diffraction

Alloys which were hard and brittle were ground to a fine powder in an agate mortar. Filings were produced of other alloys using a new file for each alloy. Diffraction patterns were obtained with cylindrical Debye-Scherrer cameras of radius 57.3 mm. using Cu-K α radiation. Exposure times were four hours. The type of film used was "KK-Industrial X-ray Film". The samples were mounted on a thin glass fibre which was dipped in "silicone" grease and rolled in the alloy filings or powder.

Diffraction lines were measured on the film with a device capable of measuring to ± 0.01 mm. It was estimated that sharp diffraction lines were measured to an accuracy of ± 0.05 mm. No absolute error could be assigned to each calculated "d-value", but an approximate measure of accuracy is provided in the customary way, by expressing the value to the number of significant figures commensurate with the estimated accuracy. Understandably the low-angle "d-values" are inherently less accurate than the high-angle "d-values". The intensities were estimated visually on an arbitrary basis of ten units, assigning "10" to the strongest reflection and " $\frac{1}{2}$ " to the weakest reflection.

The distance on the film between $\theta = 0^\circ$ and $\theta = 90^\circ$ was routinely determined for all diffraction patterns which had back reflections. The deviation from the ideal value of 180.00 mm. was small in each case (in the second decimal) and a correction for this deviation was not made. The internal standard KCl (.77) was used to obtain a correction factor for each camera (0.998 and 0.995 respectively) which was applied in calculating all those d-values from which cell edges were calculated.

For high-temperature x-ray diffraction the powder samples or filings were sealed into evacuated thin-walled quartz capillaries of 0.3 mm. diameter. The diffraction lines of aluminium (high purity) at room temperature and 300°C were used for calibrating the high-temperature camera radius. The Bragg-angle corresponding to each diffraction line was calculated from the accurately known "d-value" given in the "A.S.T.M. X-Ray Powder Diffraction File" (78,75). A "factor" was then simply calculated by which "S" the measured value would have to be multiplied to give "θ" the Bragg-angle corresponding to each diffraction line. The average value of this factor was 0.299.

The temperature of the sample in the camera was measured with chromel-alumel thermocouples which were calibrated from the melting points of pure metals. The metal samples used for calibration were contained in small quartz crucibles small enough to be placed directly in the x-ray camera furnace. The shielded thermocouple was introduced into the metal and heating and cooling curves were obtained in this fashion, and these clearly showed the melting and freezing of the "standard" samples. This direct way of calibrating the high-temperature x-ray camera was desirable and reliable, but was not easily accomplished technically. The "recorder" was calibrated in terms of the pure metals as described under "Differential Thermal Analysis".

Alloy samples were always equilibrated for at least twenty four hours at the temperature in question (in the x-ray camera furnace) before x-ray diffraction pictures were taken.

The x-ray diffraction tube was operated at 30KV and 15 mA.

Electron Probe Microanalysis

Samples, prepared as for photomicrography were coated for conduction with a thin film of carbon by evaporation in vacuum. Standards of pure indium and silver were analyzed under the following conditions with a "Norelco AMR/3" Electron Probe:

Gun Voltage 30KV

Beam Current 48 mA

Counting Time 10 sec.

Scanning speed 4μ /10 sec.

Electron beam incidence 90°

$\psi = 15^\circ$ ($\csc \psi$) = 3.86, using the $L\alpha_1$ lines of Ag

and In for analysis.

The accuracy of analysis was estimated to be 3% .

Composition Analysis

Alloys were analyzed for silver by the well-known Vollhard method (76). The samples were dissolved in 10 ml. of concentrated nitric acid, and the solutions were diluted to 250 ml. and aliquots were titrated with potassium thiocyanate solution using ferric nitrate solution as indicator. Pure silver metal was used as a standard.

Ternary samples were also analyzed polarographically for indium and aluminium. The samples were dissolved as before and "made up" with 0.1F sodium acetate solution to an accurately known volume to give a concentration of the respective metal ions in the range of $10^{-3}M$ to $10^{-4}M$. The sodium acetate served as a buffer and as a supporting electrolyte. A few drops of HCl solution were added prior to analysis to remove the small concentration of silver ion from the solution which for unknown reasons interfered with the analysis if left in solution. A few drops of 0.01 per cent gelatine solution were added as a "maximum suppressor". Well-defined polarographic waves of indium and aluminium were obtained in this fashion. The graphical procedure of extrapolating the polarogram plateau and drawing a vertical through the mid-point of the wave was used to measure the diffusion current which is directly proportional to concentration. Synthetic ternary samples of well-known composition were used as "standards". The uncertainty in the analysis by the polarographic method is considered to be 1.5 per cent (by wt.) in each component or 3.0 per cent in the total composition of the alloy. Silver was determined separately by the Vollhard method (76). It is well known that the latter method is capable of high accuracy under optimum

conditions. The uncertainty in the silver determination was estimated to be three parts per thousand.

THE BINARY SYSTEM SILVER-INDIUM:

RESULTS AND DISCUSSION

TABLE 1

ANNEALING HISTORY AND COMPOSITION OF BINARY ALLOYS

INDIUM-SILVER

Alloy No.	Composition % Ag	Time of Annealing Hours	Annealing Temperature °C	Quenched from Temperature of °C (in liquid nitrogen)
1	76.69	168	655	655
2	72.11	168	655	655
3	68.68	168	655	655
4	76.69	168	655	655
		168	500	500
5	72.11	168	655	
		168	500	500
6	68.68	168	655	
		168	500	500
	76.69	168	655	
7		168	500	
		168	325	325
	72.11	168	655	
8		168	500	
		168	325	325
	68.68	168	655	
9		168	500	
		168	325	325
	66.50	168	655	
10		168	500	
		168	325	
		90	360	360
11	76.69	168	325	
		336	165	165
12	70.15	168	325	
		336	165	
13	68.68	168	325	
		336	165	165
14	76.69	168	325	
		504	129	
15	73.82	168	325	
		504	129	
16	72.11	168	325	
		504	129	
17	70.15	168	325	
		504	129	
18	68.68	168	325	
		504	129	

Table 1 Continued

Alloy No.	Composition % Ag	Time of Annealing Hours	Annealing Temperature °C	Quenched from Temperature of °C (in liquid nitrogen)
19	66.50	168	325	
		504	129	
20	65.28	168	325	
		504	129	
21	62.85	336	135	
22	62.50	336	135	
23	61.04	336	135	
24	34.00	336	135	
25	36.04	672	135	
26	33.89	672	135	
27	31.97	672	135	
28	62.85	168	275	275
29	55.63	168	325	325
30	55.63	168	275	275
31	55.63	168	225	225
32	55.63	336	135	

Differential Thermal Analysis

The system was investigated in the region from pure indium to 75 per cent silver. The region 100-75 per cent silver was well established previously (61,6) and was not investigated by me in this work.

The D.T.A. data are presented in Tables 2 and 3, in the temperature ranges 700 to 400°C and 300°C to room temperature, respectively. The column headings in those tables indicate the type of transformation responsible for the thermal effect observed at the temperature given.

In order to be able to present the phase diagram on a sufficiently expanded scale, it is presented in two parts in the temperature range 700° to 400°C and 300°C to room temperature as given in Figs. 13, and 14.

The liquidus determined in the present investigation agrees with that of Weibke and Eggers (61) very well, below 450°C. At higher temperatures the agreement is not so good, with the presently determined liquidus lying approximately 8°C higher. The small number of points indicated by "X" in the phase diagram of Fig. 13, indicate the liquidus of Weibke and Eggers.

The homogeneous γ -phase region was found to extend to much higher indium concentration than previously established by Weibke and Eggers (61), as is evident by comparing the two phase diagrams in Fig. 13, and Fig. 1, respectively. The high-temperature γ -solidus was established by D.T.A., Table 2, and the low-temperature γ -solidus was determined on the basis of x-ray diffraction data of alloys Nos. 28,29,30,31 (Table 10), and by extrapolation of the high-temperature experimental data.

No isothermal arrest was observed at 281°C by differential

TABLE 2
DIFFERENTIAL THERMAL ANALYSIS DATA OF SILVER-INDIUM ALLOYS
IN THE TEMPERATURE RANGE 700°C-300°C

Wt% Ag	Liquidus °C	Isotherm $\alpha + L \rightarrow \beta$ °C	Isotherm $\beta + \alpha \rightarrow \gamma$ °C	Isotherm $\beta \rightarrow \gamma + L$ °C	Solidus of γ °C	°C
75.00		696	669			
74.00		697	670			$(\alpha + \gamma)/\gamma$
73.00		694	670			659
72.00		695	673			$(\gamma + \beta)/\gamma$
71.00		692				665
70.00		690				663
				662		
69.00	695	688		660		$(\beta + L)/\beta$
68.00	683			659	650	669
67.00	666			658	647	
66.00	650				642	
65.00	648				627	
64.00	641				612	
63.00	633				592	
62.00	618				558	
61.00	614				580	
60.00	608					
59.00	595				547	
58.00	592					
57.00	580					
56.00	572					
55.00	561					
52.00	544					
48.00	511				448	
43.00	473					

Table 2 (Continued)

Wt% Ag	Liquidus °C	Isotherm $\alpha + L \rightarrow \beta$ °C	Isotherm $\beta + \alpha \rightarrow \gamma$ °C	Isotherm $\beta \rightarrow \gamma + L$ °C	Solidus of γ °C	°C
38.00	442					
33.01	410					
27.01	374					
24.99	366					
24.00	359					
23.00	353					
22.00	346					
20.99	342					
20.00	333					
18.00	319					
16.00	301					

TABLE 3

DIFFERENTIAL THERMAL ANALYSIS DATA OF SILVER-INDIUM ALLOYS

IN THE TEMPERATURE RANGE 300°C-100°C

Wt% Ag	Isotherm $\gamma \rightarrow \epsilon + L$ °C	Isotherm $\epsilon + L \rightarrow \phi$ °C	Isotherm $L \rightarrow \phi + \text{In}$ °C	$\gamma/(\gamma + \epsilon)$ °C	°C
73.00					$\gamma/(\gamma + \alpha)$
69.00					145
68.00				200	
67.00				254	
				280	
				224	
66.00				296	
64.00	205	165	144	292	
63.00	206	166	144	294	
62.00	205	167	144	282	
61.00	205	165	144	282	
60.00	207	166	145	276	
59.00		166	144		
58.00	204	165	143		
57.00		168	144		
56.00		167	144		
55.00	202	164	144		
52.00	205	164	143		
48.00	202	165	145		
43.00	202	161	143		
38.00	203	163	143		
33.01	204	162	144		
27.01	202	159	143		

Table 3 (Continued)

Wt% Ag	Liquidus °C	Isotherm $\epsilon + L \rightarrow \phi$ °C	Isotherm $L \rightarrow \phi + In$ °C
24.99		164	144
24.00		165	144
23.00		164	144
22.00		163	144
20.99		164	144
20.00		163	144
18.00		164	144
16.00		164	144
14.00	286	161	144
12.00	266	163	142
10.00	244	162	144
9.00	234	163	144
8.01	224	154	144
7.02	210	154	144
6.02	193	156	144
4.99	177	151	143
3.99	156	147	143
3.52	149		143
3.01	144		144
2.50	144		143
1.54	147		143
1.00	150		142
0.55	153		143

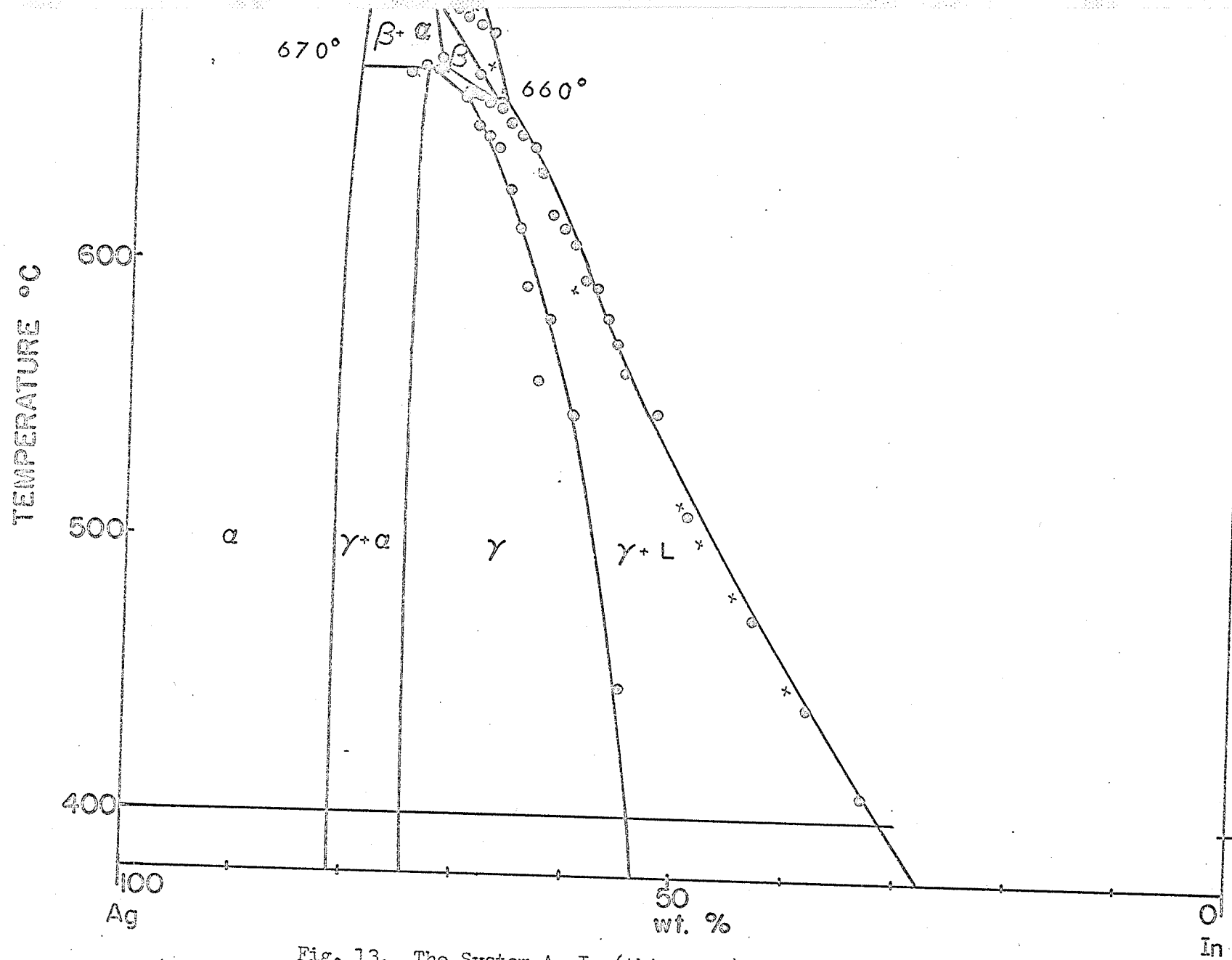


Fig. 13. The System Ag-In (this work) in the range 400°C-700°C.

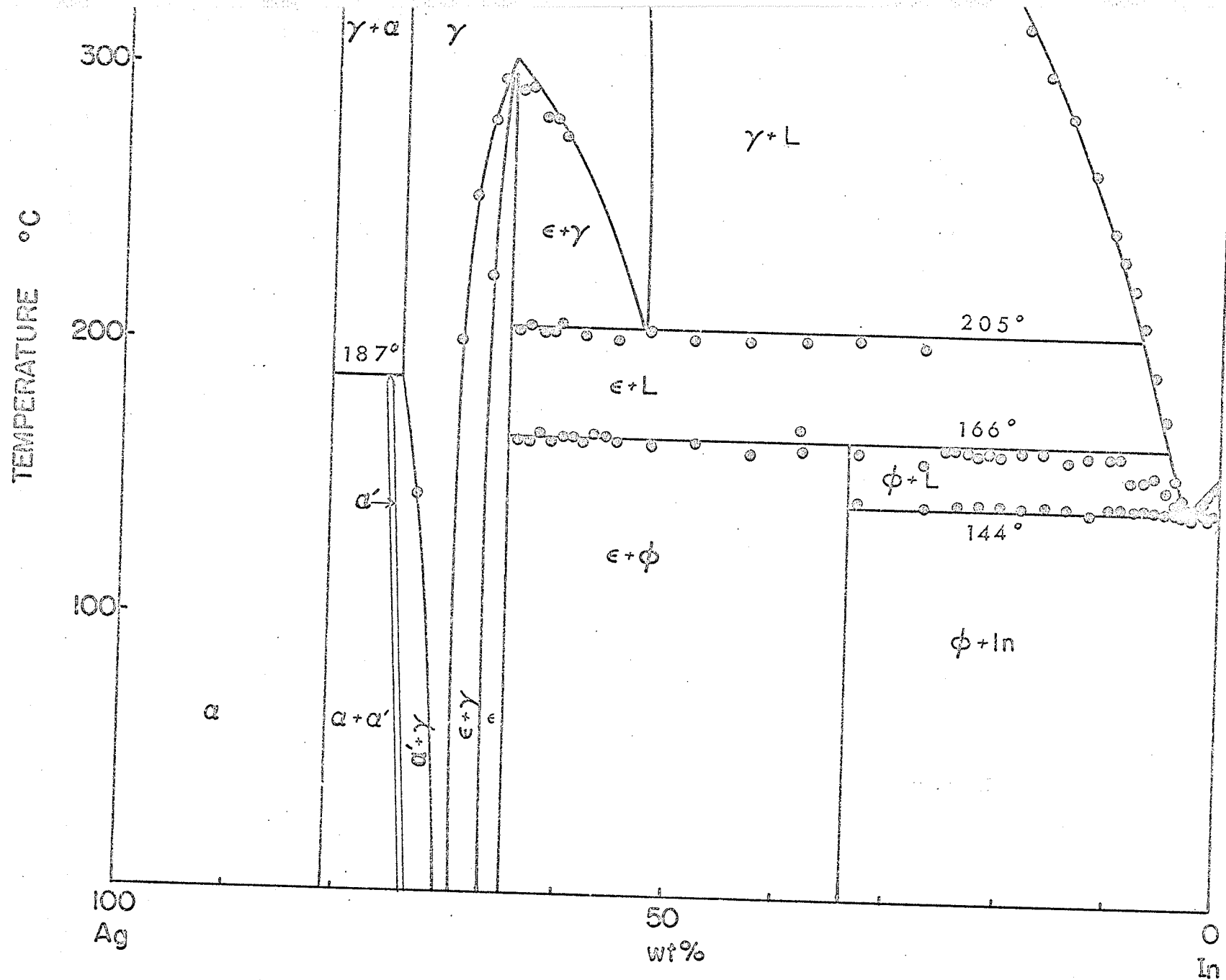


Fig. 14. The System Ag-In (this work) below 300°C

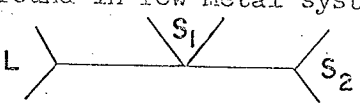
thermal analysis. This observation is in accord with x-ray diffraction data which show that the γ -phase exists as an equilibrium phase below 281°C . If the 281°C "isotherm" really existed but was simply not observed, then a new fourth intermediate phase would also have to exist in accordance with phase rule. Such a new intermediate phase does not exist.

An examination of the published data of Von F. Weibke and H. Eggers (61) shows that almost all the "heat effects" which they observed and which they attributed to the constant temperature reaction 281°C occur close to the ϵ -phase region. In the present investigation these "heat effects" were also observed (Table 3) but they did not occur at constant temperature with changing composition, neither were the "peaks" on the thermogram characteristic of an isothermal transformation. These "heat effects" are due to the transformation $\gamma \rightarrow \epsilon$ as could be shown by x-ray diffraction (Table 10). No experimental basis exists for a constant temperature transformation at 281°C .

On the silver-rich side of the ϵ -phase the same authors (61) observed similar heat effects which they attributed to an order-disorder transformation of the γ -phase. In the present investigation these "heat effects" were also observed but again it was shown by x-ray diffraction (Table 9) that they were due to the $\gamma \rightarrow \epsilon$ transformation. Above the temperature at which the "heat effects" occurred only γ -phase was present, slightly below this temperature γ and ϵ phases were present. No experimental evidence exists for claiming the order-disorder transformation shown in the previously published phase-diagrams (61,29).

I redetermined all other "isotherms" given by Von F. Weibke and H. Eggers (61), except one. The results agree within three degrees as can be seen from the values given below. The temperatures in parentheses are those of Weibke and Eggers (61).

144°C	(141°C)	Eutectic
166°C	(166°C)	Peritectic
205°C	(204°C)	Metatectic*
660°C	(660°C)	Metatectic
670°C	(667°C)	Peritectoid
695°C	(693°C)	Peritectic

* A rare case found in few metal systems. The transformation in general is as follows:  i.e. A solid partially melts as the temperature falls. This transformation will be called "metatectic".(64) But, the latter name has sometimes been applied to a peritectoid reaction.

It will be noted that the relatively rare metatectic reaction in which a solid phase partially melts on lowering the temperature occurs twice in this system. The 205°C "metatectic" reaction manifests itself as inter-grain liquefaction of alloys which are rapidly cooled from above 205°C. More is said about this under "The γ -phase and Adjoining Regions".

In Table 3, it will be noted that the eutectic "temperature halt" at 144°C is also recorded at compositions where it should not occur, viz. those lying between the ϵ -phase and the ϕ -phase. Nevertheless they were observed to occur (not as spurious phenomena), and were recorded as such. The occurrence of these 144°C-differential thermal analysis peaks in alloys of a composition at which they should not occur under equilibrium conditions

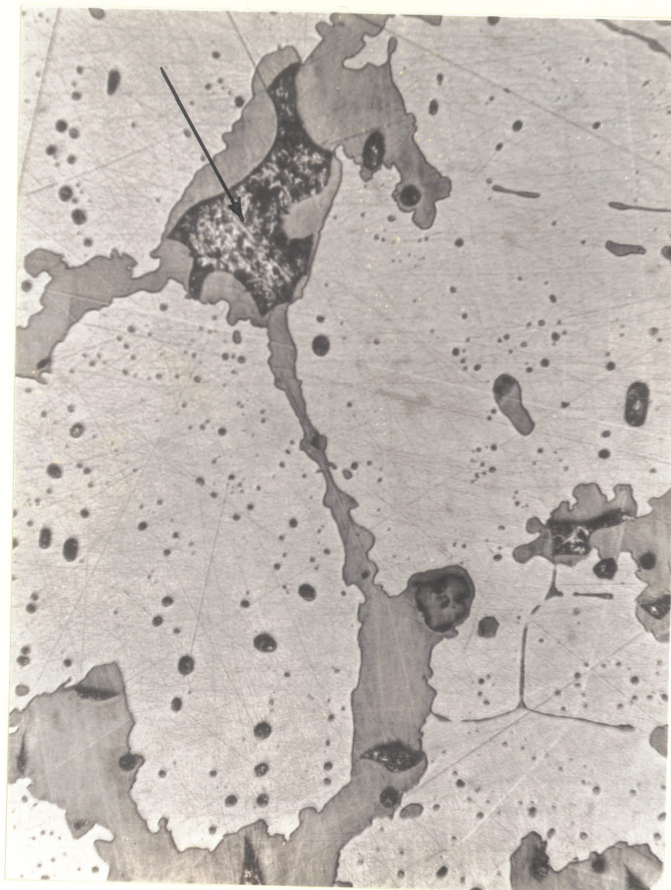


PLATE 1

ALLOY NO. 23 COMPOSITION 61.04% Ag

Magnification approx. 100X. "Trapped"
In-Phase (Dark Grey at top). Can be
seen surrounded by ϕ -phase. Major con-
stituent is ϵ -phase.

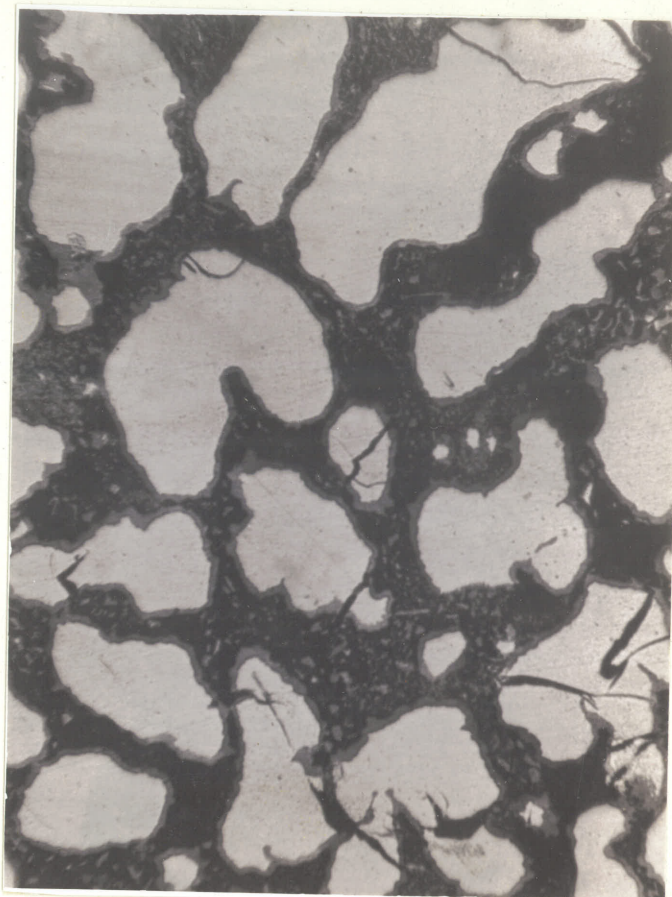


PLATE 2

COMPOSITION 34.00% Ag

After Differential Thermal Analysis
with no further annealing.
Magnification approx. 80X. Reaction
rim of δ -phase surrounding the "is-
lands" of γ -phase (light area) can be
seen.

is due to the presence of metastable liquid (metastable with respect to composition) which then freezes at its normal freezing temperature of 144°C when that temperature is reached on cooling, giving rise to the observed eutectic transformation at its normal temperature of 144°C . Non-equilibrium states bring about in this case a lengthening of the 144°C eutectic isotherm as determined experimentally, and this will occur even with very slow cooling rates, since the time necessary to establish equilibrium would amount to months of annealing. The photomicrograph (Plate 1) shows the "trapped" eutectic (surrounded by ϕ -phase), which exists metastably, and is responsible for the 144°C -peak. Plate 2, shows an alloy that was subjected to differential thermal analysis only and no additional heat treatment. The substantial amount of γ -phase (metastable) surrounded by a narrow "rim" of ϕ -phase (gray) and the substantial amount of dark gray indium-rich matrix are clearly visible. After annealing below a temperature of 166°C (Plate 14, page no. 134) the amount of γ -phase has clearly diminished as well as the amount of indium-rich matrix, while the ϕ -phase "reaction rim" has increased in amount. Since the γ -phase is disappearing with time and since it is not in physical contact with the matrix it is metastable with respect to the matrix and the ϕ -phase.

Electron Probe Microanalysis

Referring to Plate 3, the microanalysis of alloy number 24, of overall composition 34.00 per cent silver was as follows:

areas AB, EF, GH, KL had the same composition -- 33.2 per cent silver.

The "reaction zone" BC, DE, HJ have essentially the same composition as the areas surrounding them, i.e. 33.0 per cent silver.

The "islands" CD, JK had an average composition of 70.6 per cent silver.

Due to heterogeneity and surface unevenness the area FG (matrix) could not be analyzed quantitatively. Qualitatively it was established that it was nearly pure indium. Within experimental error, the composition of the areas "AB, EF, GH, KL" and the reaction "rims" corresponded to the composition of the ϕ -phase (Ag In_2) and the "islands" had a composition (average) corresponding to the γ -phase.

The analysis of an alloy of overall composition 66.50 per cent silver (Alloy No. 10) yielded slightly higher results for the bright areas in Plate 6, but this was not significant, considering the magnitude of the experimental error.

Referring to Plate 4, the microanalysis of alloy 22 of overall composition 62.50 per cent silver was as follows: areas "AB, EF" had the same composition, viz. 66.1 per cent silver. The areas "BC, DE" both contained 32.3 per cent silver. The area "CD" showed discoloration under the microscope, presumably due to oxidation and no meaningful results could be obtained for this area.

CHARACTERISTIC X - RAY PICTURE
OF ELECTRON PROBE SCAN
MAG. APPROX. 350 X
COMPOSITION : 34.00 % Ag (by weight)

90

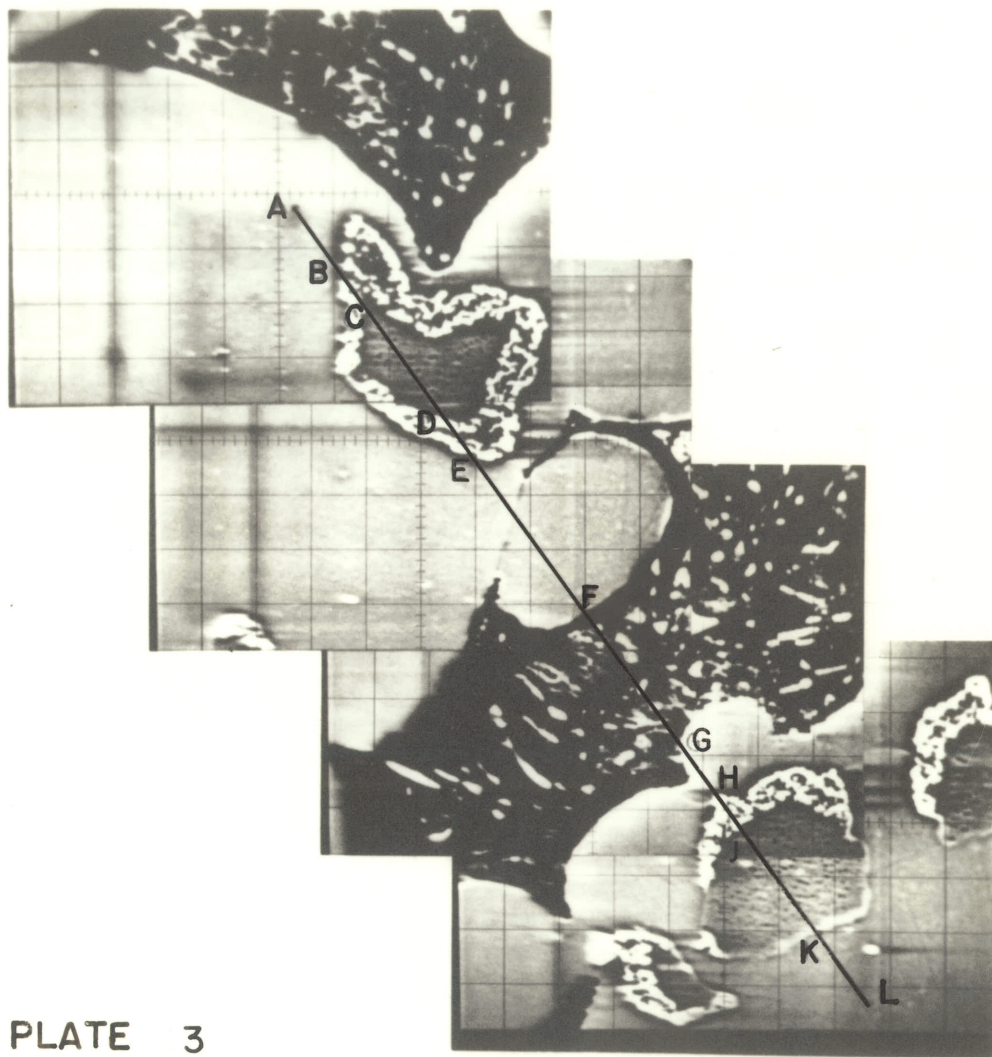


PLATE 3

CHARACTERISTIC X-RAY PICTURE
OF ELECTRON PROBE SCAN

91

MAG. APPROX. 350 X

ALLOY NO. 22

COMPOSITION: 62.50 % Ag (by weight)

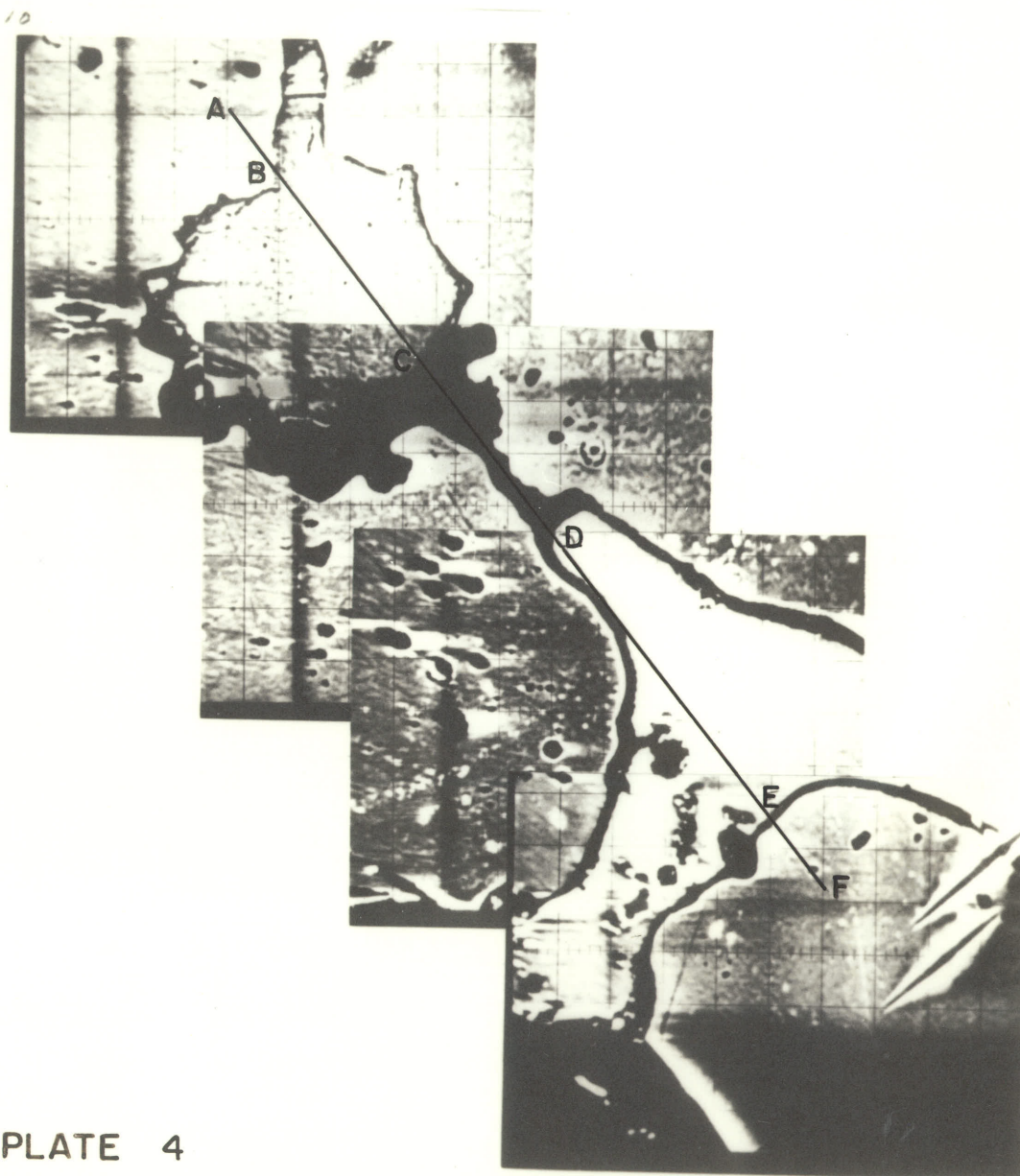


PLATE 4

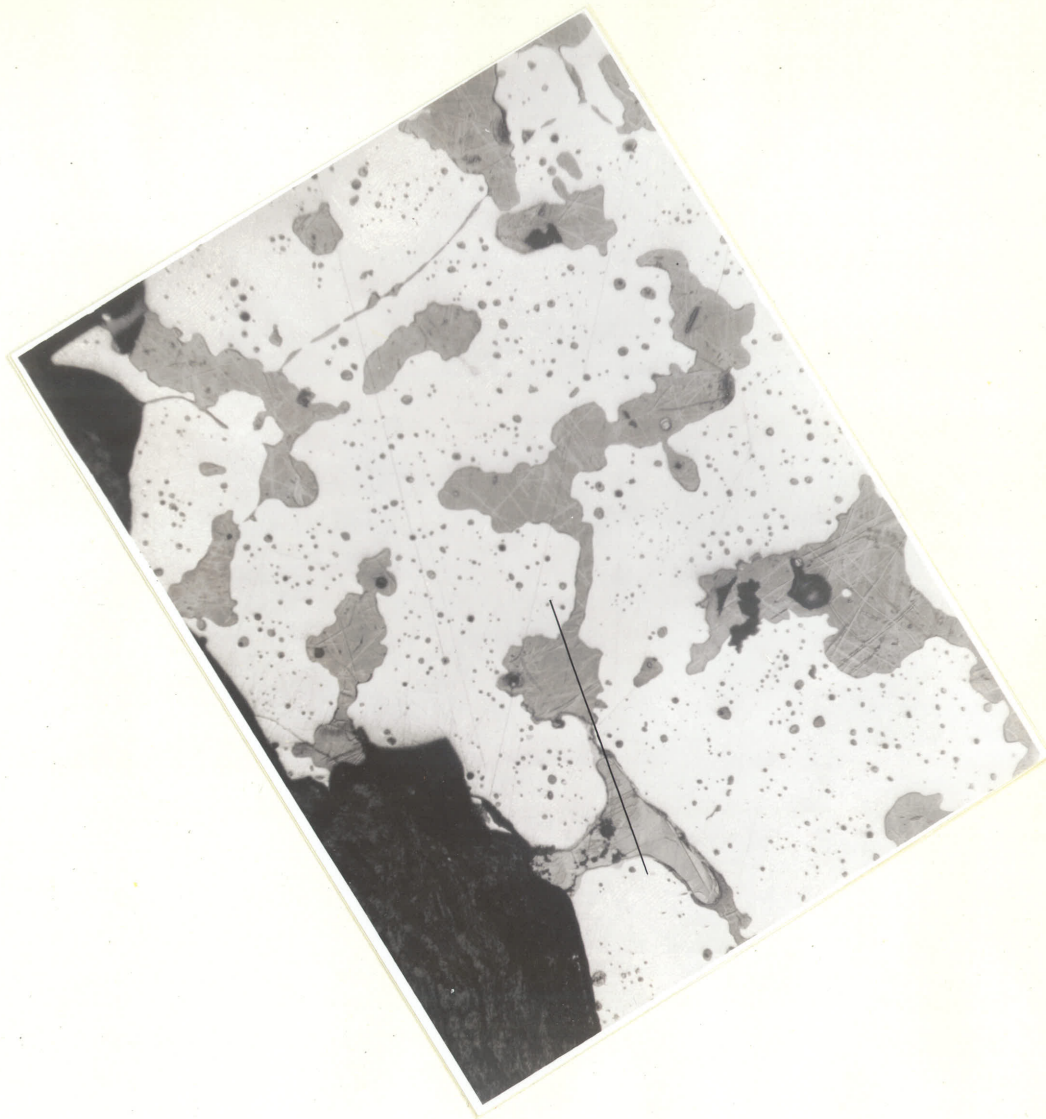


PLATE 5

ALLOY NO. 22 COMPOSITION 62.50% Ag

Magnification approx. 100X. Areas of ϕ -phase (Dark grey) are traversed by electron beam as indicated.

Within experimental error the areas analyzed "AB, EF" and "BC, DE" corresponded in composition to the ϵ -phase and the ϕ -phase respectively. Plate 5 is a photomicrograph of the same alloy as shown in Plate 4 and the same area as that analyzed by electron probe can be seen; the traverse of the electron beam is shown in the photomicrograph.

The distinct brown colour observed under the reflecting microscope of the areas showing as gray in Plate 5, which was obtained after etching with ammonium persulfate solution (34) was identified as characteristic of the ϕ -phase, after the area analyzed by electron probe was correlated with the same area under the microscope as shown in Plate 5.

The electron probe analysis results showed that an alloy of overall composition of 62.50 per cent silver consisted at room temperature of the stable phases " ϵ " and " ϕ " as expected, and that an alloy of overall composition of 34.00 per cent silver consisted of the stable phase " ϕ ", an indium rich matrix and the metastable γ -phase, which exists at room temperature even after prolonged annealing at a temperature at which this phase is not stable. The metastable γ -phase (islands) Plate 3 is surrounded by a zone of ϕ -phase. The latter phase increases with time while the γ -phase decreases with time.

Within the error range of the electron probe, the composition of the ϕ -phase can be designated as AgIn_2 (31.97 % Ag) as suggested by Hellner (29) though more accurate analysis may reveal that the composition of the ϕ -phase does not correspond to any simple formula. Since the composition of the ϕ -phase is AgIn_2 , or nearly that, an alloy of overall composition of

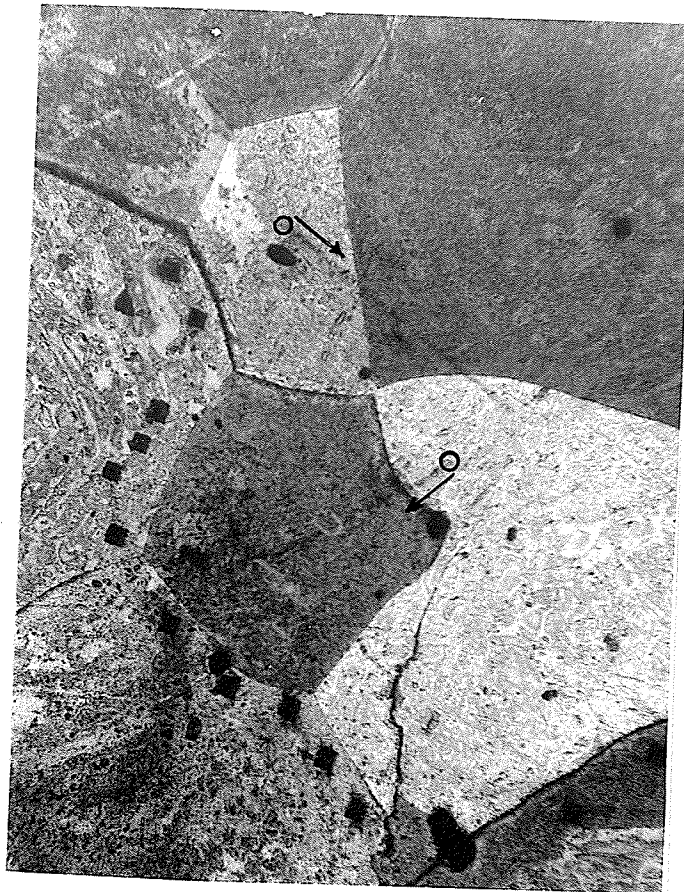


PLATE 6

ALLOY NO. 10 COMPOSITION 66.50% Ag.
QUENCHED FROM 360°C

Magnification Approx. 100X. Faint
streaks (indicated by arrows) show
where electron beam traversed.

34.00 per cent silver must be heterogeneous ($\epsilon + \phi$) at equilibrium at room temperature, and this means that the "reaction zone" formed around the "islands" of γ -phase in Plate 3 should be heterogeneous, consisting of a small amount of ϵ -phase and a large amount of ϕ -phase. The spotty nature of the "reaction zone" revealed by the electron probe "scan-picture" in Plate 3, may be due to such heterogeneity although microscopic observation does not reveal any heterogeneity in the "reaction zone". Since the amount of ϵ -phase in the "reaction zone" would necessarily be small, the average composition of the "reaction zone" determined with the electron probe would be that of the ϕ -phase within the error of the instrument.

Plate 14 is a photomicrograph of the same alloy-sample as that shown in the electron probe "scan-picture" of Plate 3, though the two corresponding areas are not exactly the same. The photomicrograph is included, to show how the appearance of phases under the microscope was correlated with composition of phases.

Plate 6 is a photomicrograph of alloy No. 10, of overall composition 66.50 per cent silver; it shows the exact areas analyzed with the electron probe. Two electron beam traverses, visible as faint streaks, can be seen originating in the respective areas as indicated in the photomicrograph. It was of interest to know whether the dark and bright areas represent different phases or simply different grain orientations of the same phase. The slightly higher silver content of the brighter areas, as obtained by electron probe microanalysis, is attributable to the greater dissolution of indium by the etching reagent relative to silver. The conclusion was reached that different grain orientations of the same phase are present.

TABLE 4

INTERPLANAR SPACINGS (d) OF SILVER-INDIUM ALLOYS

(ANNEALED AT 129°C, 21 DAYS)

hk.l (γ -Phase)	Calculated* (γ -Phase)	Alloy No. 17 70.15% Ag ($\gamma+\epsilon$)	Alloy No. 18 68.68% Ag ($\gamma+\epsilon$)	Alloy No. 19 66.50% Ag (ϵ)	Alloy No. 20 65.28% Ag (ϵ)	Calculated** (ϵ -Phase)	hkl ϵ -Phase
	d(Å)	I d(Å)	I d(Å)	I d(Å)	I d(Å)	d(Å)	
00.1	4.79						
				1	2.84	2.98	3 3 1
				1	2.632	2.85	2 2 2
10.0	2.553	4	2.556	6	2.556	2.642	3 2 1
00.2	2.397	5	2.387	4	2.391		
		3	2.326	9	2.325		
10.1	2.253	10	2.263	10	2.255	2.330	4 1 1
				0.5	2.103		
				1	2.097	2.107	3 3 2
				0.5	2.023	2.018	4 2 2
				0.5	1.937	1.939	5 1 0
				0.5	1.802	1.805	5 2 1
10.2	1.748	4	1.749	5	1.746		
				3	1.645		
00.3	1.598			3	1.645	1.6475	6 0 0
11.0	1.474	3	1.481	0.5	1.601	1.6036	6 1 1
				1	1.457		
				1	1.425	1.4575	6 3 1
11.1	1.409			1	1.424	1.4268	4 4 4
				0.5	1.395		
10.3	1.355	6	1.354	7	1.354	1.3980	7 1 0
		0.5	1.344	7	1.343		
20.0	1.277			8	1.344	1.3452	7 2 1
11.2	1.256	5	1.259	6	1.258		
20.1	1.234	2	1.239	3	1.237	1.2554	7 3 2
		0.5	1.215	3	1.216		
00.4	1.1985	1	1.195	2	1.197	1.2168	8 1 1
				0.5	1.199	1.1987	8 2 0
				0.5	1.180	1.1815	6 5 3

%

Table 4 (Continued)

hkl (γ -Phase)	Calculated* (γ -Phase)	Alloy No.17 70.15% Ag ($\gamma+\epsilon$)		Alloy No.18 68.68% Ag ($\gamma+\epsilon$)		Alloy No.19 66.50% (ϵ)		Alloy No.20 65.28% Ag (ϵ)		Calculated** (ϵ -Phase)	hkl ϵ -Phase
20.2	1.1267	0.5	1.129	1	1.165	3	1.165	1	1.163	1.1650	8 2 2
10.4	1.0849					0.5	1.148			1.1491	8 3 1
11.3	1.0835	0.5	1.0825	1	1.130	1	1.133	0.5	1.132	1.1339	6 6 2
20.3	0.9974	3	0.9979	0.5		0.5	1.119			1.1193	7 5 2
21.0	0.9650			0.5		0.5	1.091			1.0916	9 1 0
21.1	0.9460	3	0.9492	1	1.0335						
11.4	0.9299	4	0.9298	0.5	1.0408	2	1.0415	2	1.0415	1.0420	9 3 0
				4	0.9976	3	0.9976	3	0.9984	0.9985	9 4 1
				0.5	0.9789	3	0.9778	3	0.9782	0.9788	10 1 1
21.2	0.8951	4	0.8959			1	0.9595	1	0.9511	0.9512	10 2 2
20.4	0.8737			5	0.9491						
30.0	0.8510			4	0.9300						
30.1	0.8379			2	0.9252	4	0.9259	4	0.9262	0.9258	8 7 1
21.3	0.8260	6	0.8283	1	0.8958	1	0.9023	2	0.9028	0.9024	10 4 2
				2	0.8803	5	0.8809	5	0.8815	0.8806	11 2 1
				1	0.8738	0.5	0.8739	0.5	0.8748	0.8737	8 8 0
				1	0.8605	2	0.8609	2	0.8613	0.8604	10 4 4
				2	0.8541	2	0.8543	2	0.8550	0.8539	11 3 2
						0.5	0.8302	0.5	0.8305	0.8295	9 6 5
				4	0.8279						
				2	0.8180	3	0.8186	4	0.8192	0.8181	12 1 1
30.2	0.8020	1	0.8071	4	0.8071	5	0.8078	5	0.8083	0.8071	11 5 2
		1	0.7976	0.5	0.7978						
				0.5	0.7865	2	0.7871	1	0.7875	0.7864	11 6 1
				4	0.7766	4	0.7772	3	0.7777	0.7766	12 3 3
using $a = 2.961 \text{ \AA}$, $c = 4.778 \text{ \AA}$											

* using $a = 2.961 \text{ \AA}$, $c = 4.778 \text{ \AA}$ ** using $a_0 = 9.887 \text{ \AA}$

The ϵ -Phase and Adjoining Regions

From Table 4, it is evident that alloy No. 18 of composition 68.68 per cent is heterogeneous, consisting of ($\gamma + \epsilon$) phases, since lines from both phases appear strongly in the diffraction pattern of this alloy. Alloy No. 19 of composition 66.50 per cent silver is homogeneous ϵ -phase. From the respective intensities of diffraction lines of the ϵ -phase and of the γ -phase in the homogeneous and heterogeneous alloys it is estimated that the boundary of the ϵ -phase on the silver-rich side lies at 67.5 per cent silver. In the same Table it is seen that the alloy of 70.15 per cent silver still contains small amounts of ϵ -phase. Since only the four strongest lines of the ϵ -phase appear in this alloy, the ϵ -phase is present at a concentration near the limit of detection (by this means). The ϵ -phase is estimated to be present in this alloy at a concentration of four to five per cent, and this places the indium-rich boundary of the γ -phase at approximately 70.3 per cent silver at room temperature, as shown in Fig. 14, page 83.

Alloys of composition 65.28 and 66.50 per cent silver respectively are both homogeneous (ϵ) as shown by x-ray diffraction data in Table 4. Neither was any second phase observed in these two alloys under the microscope.

An alloy of composition 62.85 per cent silver (Table 5) is heterogeneous, and consists of ($\phi + \epsilon$) phases. The small amount of ϕ -phase present in this alloy was also observed under the microscope as shown in Plate 7. Therefore, the indium-rich boundary of the ϵ -phase must be between

TABLE 5

INTERPLANAR SPACINGS (d) OF SILVER-INDIUM ALLOYS

(ANNEALED AT 135°C, 14 DAYS)

hkl ε-Phase	Alloy No. 19 66.50% Ag ε-Phase		Alloy No. 21 62.85% Ag (ε+δ)		Alloy No. 32 55.63% Ag ε+δ		Alloy No. 24* 34.00% Ag δ-Phase		hkl δ-Phase
	I	d(Å)	I	d(Å)	I	d(Å)	I	d(Å)	
222	1	2.84	0.5	2.84	0.5	2.85			
			0.5	2.679			0.5	2.83	002
321	1	2.632	0.5	2.624	1	2.692	10	2.695	211
					1	2.634			
411	10	2.323			0.5	2.425	5	2.429	220
			10	2.321	10	2.331			
			0.5	2.167	1	2.172	8	2.172	310
332	1	2.097	1	2.104	1	2.105			
422	0.5	2.010	0.5	2.013	0.5	2.018			
510	0.5	1.933	0.5	1.933	1	1.942			
521	0.5	1.800			0.5	1.808			
600	3	1.645	3	1.648	4	1.650			
611			0.5	1.599	0.5	1.598	4	1.597	411
							1	1.536	420
					1	1.463	3	1.466	402
631	1	1.457	0.5	1.458					
444	1	1.425	1	1.428	1	1.431			
							5	1.402	332
710	1	1.395	1	1.399	1	1.398			
721	8	1.344	8	1.345	8	1.349			
732	0.5	1.254	0.5	1.255					
							2	1.244	521
811	6	1.217	5	1.217	5	1.220			
							2	1.214	440
							3	1.178	413
822	3	1.165	2	1.165	1	1.167			

* Microanalysis of δ-phase only.

Table 5 (Continued)

hkl €-Phase	Alloy No. 19 66.50% Ag €-Phase	Alloy No. 21 62.85% Ag (€+Ø)	Alloy No. 32 55.63% Ag €+Ø	Alloy No. 24* 34.00% Ag Ø-Phase	hkl Ø-Phase
662	1 1.133	0.5 1.133	0.5 1.134		
930	2 1.0415	1 1.0418	1 1.0428	4 1.0540	523
941	3 0.9976	2 0.9980	3 0.9986	1 1.0344	424
10·1·1	3 0.9812	1 0.9786	3 0.9791		
10 2 2	1 0.9505	1 0.9515	1 0.9516		
871	4 0.9259	4 0.9263	4 0.9266	1 0.9321	543
10·4·2	1 0.9023	3 0.9030	3 0.9034	3 0.9209	335
11·2·1	5 0.8809	5 0.8814	5 0.8817	4 0.9035	642
880	0.5 0.8739	1 0.8745	0.5 0.8752	1 0.8881	604
10·4·4	2 0.8609	2 0.8612	3 0.8617		
11·3·2	2 0.8543	2 0.8550	3 0.8552		
965	0.5 0.8302	1 0.8307	0.5 0.8312	2 0.8441	811
12·1·1	3 0.8186	3 0.8192	4 0.8194	3 0.8225	445
11·5·2	5 0.8078	5 0.8082	6 0.8086	3 0.8110	535
11·6·1	2 0.7871	3 0.7876	4 0.7878	0.5 0.7998	605
12·3·3	4 0.7772	4 0.7778	5 0.7780	7 0.7766	743



PLATE 7

ALLOY NO. 21 COMPOSITION 62.85% Ag
ANNEALED TWO WEEKS AT 135°C

Magnification 100X. Small amount of ϕ -phase (Darker areas) is still present. The main constituent is ξ -phase. A very small amount of "trapped" In-phase within the ϕ -phase is also present.

65.28 and 62.85 per cent silver. It is estimated to lie at 65.0 per cent silver. The boundary concentrations quoted are for 129°C but since these boundaries are very nearly vertical in the temperature range 129°C to room temperature the boundaries will lie at approximately the same concentrations at room temperature. The extent of the homogeneous ϵ -phase region is approximately 2.5 per cent at room temperature. The "compound" Ag_2In has a composition 65.28 per cent silver, which is within the homogeneous ϵ -phase range as Hellner (29) had found, but in view of the variable composition of the ϵ -phase one can hardly speak of a compound within this composition range, nor can one identify the ϵ -phase with the composition Ag_2In as implied by Hellner (29); he stated that the ϵ -phase has a composition Ag_2In . Weibke and Eggers estimated the composition of the ϵ -phase to be 66.9 to 66.5 per cent compared to 67.5 to 65.0 per cent silver found in the present investigation.

It has been shown that the ϵ -phase is not a stoichiometric compound but exists over a range of composition. In other words, the basic cubic primitive lattice of the ϵ -phase will tolerate a variation in the concentration of indium and silver atoms with a consequent lattice parameter variation.

The alloy of composition 62.85 per cent silver (Alloy No. 21) is heterogeneous (Table 5). Hence, the ϵ -phase present in this alloy has a composition corresponding to the composition of the indium-rich phase boundary, viz. 65.0 per cent silver. The d -values (Table 5) of this alloy belonging to the ϵ -phase in the range $1.645^{\circ} \geq d \geq 0.9252^{\circ}$ were

used to calculate the lattice parameter, from the equation $d = \frac{a}{(h^2 + k^2 + l^2)^{1/2}}$ using the corresponding (hkl) values given by Hellner (29). The alloy of composition 68.68 per cent silver (Alloy No. 18) Table 4, is heterogeneous ($\gamma + \epsilon$). The d-values (in the same range) belonging to the ϵ -phase were used to calculate the lattice parameter at the composition of the silver-rich phase boundary of the ϵ -phase, viz. 67.5 per cent silver.

$a = (9.887 \pm 0.004) \text{ \AA}$ at 65.0 per cent silver

$a = (9.878 \pm 0.004) \text{ \AA}$ at 67.5 per cent silver.

The errors represent the mean deviation.

The value of $a_0 = (9.885 \pm 0.005) \text{ \AA}$ at the composition Ag_2In (65.28 % Ag) as determined by Hellner (29) falls within the range of values determined by me.

The $\gamma/(\gamma + \epsilon)$ boundary was established using differential thermal analysis (Table 3), and x-ray diffraction (Tables 9,10). For example, the alloy of 68.68 per cent silver (Table 9) is heterogeneous at 129°C consisting of ($\gamma + \epsilon$) phases, but is homogeneous (γ) at 165°C . Therefore the boundary $\gamma/(\gamma + \epsilon)$ must lie between 165°C and 129°C at this composition. Similarly the alloy of 55.63 per cent silver (Table 10) quenched from 325°C was homogeneous (γ) but the same alloy quenched from 225°C was heterogeneous ($\gamma + \epsilon$). Therefore, the boundary $\gamma/(\gamma + \epsilon)$ must lie between 325°C and 225°C at this composition.

Heat effects observed by differential thermal analysis (Table 3) which are due to the $\gamma/(\gamma + \epsilon)$ boundary transition were also observed by Weibke and Eggers (61) who attributed these heat effects to an order-

disorder transformation of the ϵ -phase, presumably due to lack of a better explanation, although x-ray diffraction data, as they point out, did not support this view. As shown in the present investigation these heat effects are due to a phase boundary transition. No reason exists for claiming such an order-disorder transformation. Hellner (29) introduced an order-disorder transformation in the γ -phase to explain the 187°C isotherm established by Weibke and Eggers (61): no experimental evidence exists to support this transformation. The 187°C isotherm is adequately explained when the α' -phase, which was not previously discovered, is taken into consideration. From a thermodynamic point of view no need arises to introduce such an order disorder transformation.

TABLE 6

INTERPLANAR SPACINGS (d) OF SILVER-INDIUM ALLOYS

(ANNEALED AT 129°C, 21 DAYS)

hkl (α' -Phase)	Calculated* (α' -Phase)	Alloy No. 14 76.69% Ag ($\alpha'+\gamma^*$)		Alloy No. 15 73.82% Ag ($\alpha'+\gamma$)		Alloy No. 16 72.11% Ag ($\alpha'+\gamma$)		Calculated** (γ -Phase)	hk.l (γ -Phase)
	d(Å)	I	d(Å)	I	d(Å)	I	d(Å)	d(Å)	
100	4.144	0.5	4.12	1.0	4.10			4.794	00.1
110	2.930	0.5	2.91	1.5	2.91	0.5	2.91		
		3.0	2.543	3.0	2.546	4.0	2.554	2.553	10.0
111	2.393	10.0	2.380	10.0	2.395	5.0	2.390	2.397	00.2
		5.0	2.244	9.0	2.255	10.0	2.253	2.253	10.1
200	2.072	6.0	2.066	5.0	2.072	1.0	2.067		
120	1.853	0.5	1.781	0.5	1.786				
		1.0	1.740	3.0	1.748	3.0	1.748	1.748	10.2
211	1.692								
								1.598	00.3
220	1.465	7.0	1.464	8.0	1.466	4.0	1.477	1.474	11.0
221	1.381							1.409	11.1
		2.0	1.352	4.0	1.353	5.0	1.354	1.355	10.3
310	1.310								
				0.5	1.270	0.5	1.277	1.277	20.0
311	1.250	8.0	1.249	8.0	1.251	4.0	1.256	1.256	11.2
		1.0	1.228	1.0	1.233	2.0	1.236	1.234	20.1
222	1.1954	4.0	1.195	3.0	1.196	1.0	1.196	1.1985	00.4
320	1.1493								
				0.5	1.129	0.5	1.128	1.1267	20.2
321	1.1075								
				0.5	1.0836	0.5	1.0825	1.0849	10.4
400	1.0360	1.0	1.0332	0.5	1.0350			1.0835	11.3
410	1.0051								
		1.0	0.9935	1.0	0.9963	2.0	1.0012	0.9974	20.3
411	0.9768								

Table 6 (Continued)

hkl (α' -Phase)	Calculated* (α' -Phase)	Alloy No.14 76.69% Ag ($\alpha'+\gamma^*$)		Alloy No.15 73.82% Ag ($\alpha'+\gamma$)		Alloy No.16 72.11% Ag ($\alpha'+\gamma$)		Calculated** (γ -Phase)	hk.l (γ -Phase)
331	0.9507	4.0	0.9495	4.0	0.9491	3.0	0.9476	0.9650	21.0
420	0.9266	5.0	0.9264	5.0	0.9277	4.0	0.9293	0.9460	21.1
				3.0	0.8969	6.0	0.8954	0.9299	11.4
						0.5	0.8735	0.8951	21.2
						0.5	0.8525	0.8737	20.4
422	0.8459	3.0	0.8454	3.0	0.8449	0.5	0.8458	0.8510	30.0
		0.5	0.8247	2.0	0.8265	5.0	0.8272	0.8379	30.1
								0.8260	21.3
333	0.7975	6.0	0.7978	4.0	0.7981	2.0	0.7978	0.8020	30.2

* calculated using $a_0 = 4.144 \text{ \AA}$

* indicates metastable phase

** calculated using $a = 2.961 \text{ \AA}$, $c = 4.778 \text{ \AA}$.

The α' -Phase

A primitive cubic phase designated as " α' ", which I discovered, exists below 187°C at approximately 73.8 wt. per cent silver. The identification of this phase is based on x-ray powder diffraction data. Diffraction lines with (hkl) indices which are not all even or all odd as required by an F-lattice, when indexed as the α -phase, definitely exist (Table 6) and therefore they cannot belong to the normal face-centered phase, but must belong to a primitive cubic phase which has the same cell edge as the α -phase. It was not possible to obtain the pure α' -phase. In addition to " α' " the γ -phase and possibly the α -phase were always present, but the latter phase could of course not be identified unambiguously by x-ray diffraction when α' -phase is present, since " α' " and " α " both have the same cell edge. The γ -phase is present metastably in the alloy of composition 76.69 per cent silver as discussed under "Metastable States".

The cell edge of the α' -phase (and of the α -phase) is $4.144 \pm 0.004 \text{ \AA}$, an average calculated from ten different diffraction lines in the range: $2.395 \text{ \AA} \geq d \geq 0.7981 \text{ \AA}$ of the alloy of 73.82 per cent silver. The given error is the mean deviation. Within experimental error the cell edge of the α -phase at maximum solution, $4.1447 \text{ \AA}$, as given by Owen and Roberts (51) and that of the α' -phase are the same.

Indications are that the α' -phase is an ordered form of the α -phase solid solution with the indium atoms occupying the (one) corner position (0,0,0) of the cubic cell and the silver atoms occupying the (three) face-centred positions ($0, \frac{1}{2}, \frac{1}{2}$, etc.). Such an atomic arrangement results in a

primitive cubic lattice which would account for the observed diffraction lines not allowed by the face-centred lattice. This simple structure could only have the space group symmetry $Pm\bar{3}m$. Such an atomic arrangement would also account for the equal lattice parameters of the α and α' -phases. The structure consists of two different types of atoms with different radii. On purely geometric grounds an interchange of one type of atom from the corner position, to the face-center positions and vice versa would not change the cell edge if one assumes that the spherical atoms touch along the face-diagonal in each case, which is a reasonable assumption.

The structure proposed introduces a composition restriction, namely three silver atoms to one indium atom per unit cell (73.82% Ag). It was at this composition that the diffraction lines with indices (hkl) not all odd or all even were observed to be strongest when compared with the same diffraction lines at other compositions (viz. 76.96 and 72.11% Ag) as shown in Table 6.

Since the proposed structure of the α' -phase is rather simple it was possible to calculate the intensities of some of the powder diffraction lines resulting from such an atomic arrangement, and to compare these calculated intensities with the corresponding observed intensities.

The intensities I_{hkl} were calculated using the formula $I_{hkl} = K F_{hkl}^2 C_\theta p$. "K" is a constant which was assigned arbitrarily the value of unity since only relative intensities were desired. "p" is the multiplicity factor listed for various (hkl) in Table 7. $C_\theta = \frac{1 + \cos^2 2\theta}{\sin^2 \theta \cos \theta}$ is the "geometric" polarization factor for powder diffraction, also listed in Table 7. The

values of C_θ as a function of " θ " were obtained from tables given by Henry, Lipson and Wooster (54). "F", the structure factor is given by $F_{hkl}^2 = (3 f_{Ag} A_{0, \frac{1}{2}, \frac{1}{2}} + f_{In} A_{0,0,0})^2$ where "A" is the geometric structure factor for the space group $Pm\bar{3}m$ which was evaluated for the various (hkl) indices for coordinates given by the subscripts of the respective A's. The formula for the geometric factor "A" for this space group is given in the International Tables for X-ray Crystallography (53) as:

$$A = 8 \left\{ \begin{aligned} &\cos 2\pi h x (\cos 2\pi k y \cos 2\pi l z + \cos 2\pi l y \cos 2\pi k z) \\ &+ \cos 2\pi h y (\cos 2\pi k z \cos 2\pi l x + \cos 2\pi l z \cos 2\pi k x) \\ &+ \cos 2\pi h z (\cos 2\pi k x \cos 2\pi l y + \cos 2\pi l x \cos 2\pi k y) \end{aligned} \right\}$$

It can easily be verified that for all combinations of (hkl) $A = +48$ for atoms at $x = 0, y = 0, z = 0$, and that for atoms at $x = 0, y = \frac{1}{2}, z = \frac{1}{2}$, $A = +48$ for reflections with (hkl) all even or all odd and $A = -16$ for reflections with h, k and l not all even or all odd, as shown in Table 7. The atomic scattering factors (f_0) as a function of (θ) were obtained from the graph in Fig. 15, which was constructed from data of ref. (52). In the expression F_{hkl}^2 , the factor "3" enters as a weighting factor which is determined by the composition of the unit cell. The calculated intensities are large numbers. To reduce them to a more convenient scale for the purpose of comparison with experimental intensities all calculated intensities were multiplied by " 5.13×10^{-7} " before they were entered in Table 8.

A comparison of the observed intensities and the corresponding calculated intensities of the first ten diffraction lines (Table 8) shows that the relative variations of the calculated intensities are in agreement with the relative variations of observed intensities.

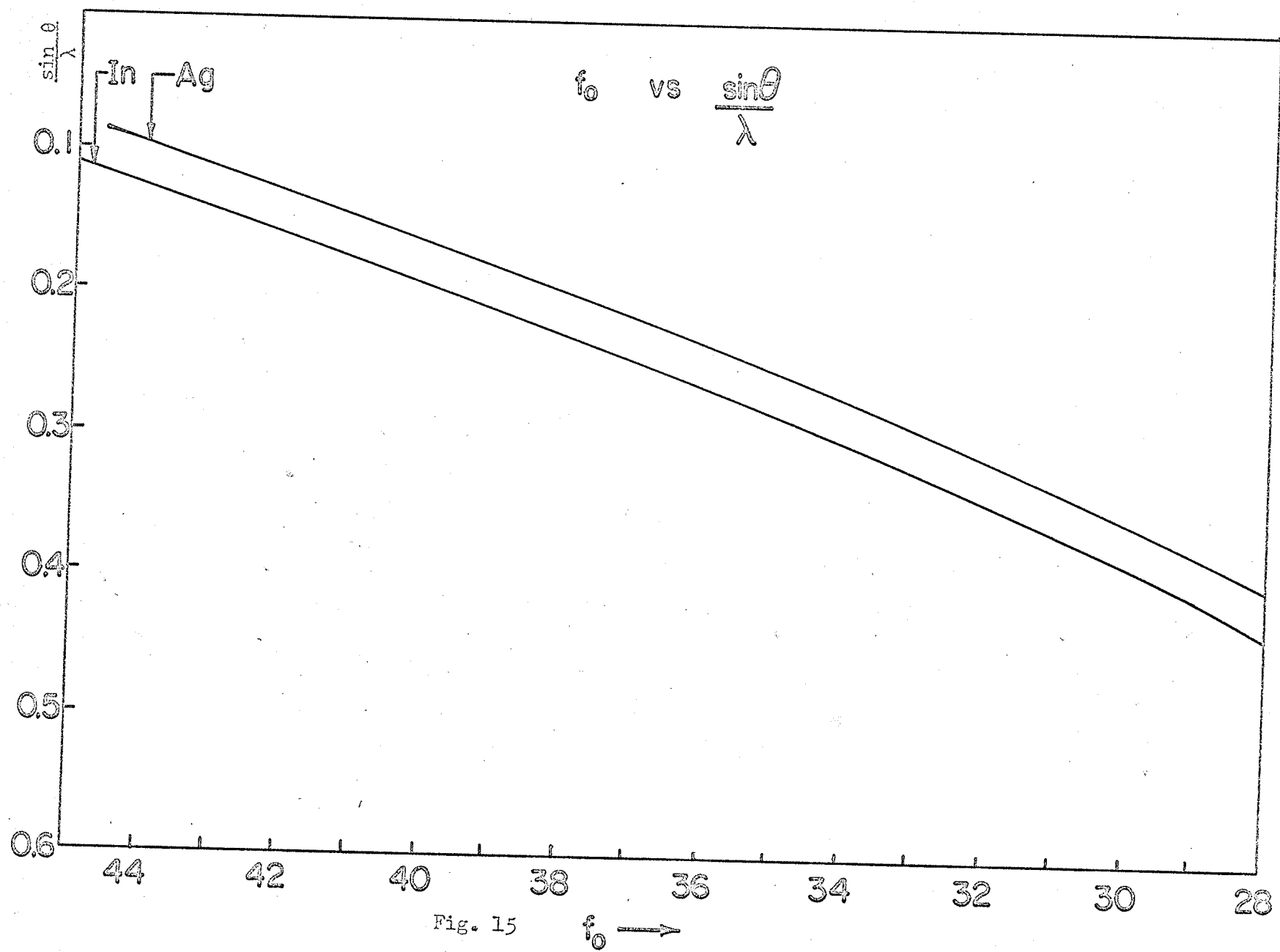


TABLE 7
DATA FOR INTENSITY CALCULATIONS OF SOME POWDER REFLECTIONS

FOR THE α' -PHASE										
hkl	$\frac{\sin \theta}{\lambda}$	C_θ	p	f_{Ag}	$A_{(0, \frac{1}{2}, \frac{1}{2})}$	f_{In}	$A_{(0,0,0)}$	F	F^2	$I = F^2 \cdot C_\theta \cdot p$
100	0.1215	54.27	6	41.45	-16	43.25	+48	86.4	7.46×10^3	0.243×10^7
110	0.1718	25.74	12	38.60	-16	40.35	+48	84.0	7.06×10^3	0.218×10^7
111	0.2104	15.98	8	36.35	+48	38.05	+48	7060.8	4.985×10^7	637.3×10^7
200	0.2430	12.98	6	34.50	+48	36.10	+48	6700.8	4.490×10^7	349.7×10^7
210	0.2716	8.727	24	32.90	-16	34.50	+48	76.8	5.90×10^3	0.124×10^7
211	0.2976	7.151	24	31.65	-16	33.10	+48	69.6	4.84×10^3	0.083×10^7
220	0.3436	5.020	12	29.35	+48	30.65	+48	5697.6	3.246×10^7	195.6×10^7
300	0.3644	4.359	6	28.45	-16	29.80	+48	64.8	4.20×10^3	0.011×10^7
310	0.3841	3.863	24	27.15	-16	28.45	+48	62.4	3.89×10^3	0.036×10^7
311	0.4029	3.486	24	26.80	+48	28.00	+48	5203.2	2.707×10^7	226.5×10^7

TABLE 8

COMPARISON OF CALCULATED AND OBSERVED

INTENSITIES (I) FOR THE α' -PHASE							
$(\alpha' + \gamma)$		γ - Phase		$(\alpha' + \alpha)$ -Phases		$(\alpha' + \gamma)$ Phases	α' -Phase
						73.82% Ag	
d (Meas.) Å	d (Calc.) Å	hkl	d (Calc.) Å	hkl	I (Obs.)	I (Calc.)*	
	4.794	00.1					
4.09			4.144	100**	10		1.25
2.92			2.930	110**	10		1.11
2.546	2.533	10.0			200		
2.395	2.397	00.2	2.393	111	1000		3269.
2.255	2.253	10.1			900		
2.072			2.072	200	500		1794.
1.786			1.853	210**	5		0.63
1.748	1.748	10.2			100		
	1.598	00.3	1.692	211**			0.43
1.466	1.474	11.3	1.465	220	700		1003.
	1.409	11.1					
			1.381	300**			0.56
1.353	1.355	10.3			150		
			1.310	310**			0.19
1.270	1.277	20.0			5		
1.251	1.256	11.2	1.250	311	750		1162.
1.233	1.234	20.1			40		
1.196	1.199	00.4	1.196	222	90		
			1.149	320**			
1.129	1.1267	20.2			20		
			1.108	321**			
	1.085	10.4					
1.084	1.084	11.3			30		

Table 8 Continued

$(\alpha' + \gamma)$		γ - Phase		$(\alpha' + \alpha)$ -Phases		$(\alpha' + \gamma)$ Phases	α' -Phase
d (Meas.) $\text{\AA}$		d (Calc.) $\text{\AA}$	hk.l	d (Calc.) $\text{\AA}$	hkl	73.82% Ag I(Obs.)	I(Calc.)*
1.0350				1.0360	400	20	
0.9963	0.9974	20.3		1.0051	410	100	
				0.9768	411		
	0.9650	21.0					
0.9491	0.9507	21.1		0.9507	331	100	
0.9277	0.9299	11.4		0.9266	420	150	
0.8969	0.8951	21.2				80	

* $I_{\text{calc.}}$ in this table = $I \times 5.13 \times 10^{-7}$ in Table 7.

** α' phase reflections permitted by P-lattice but not permitted by the F-lattice of the α phase

W means Wide line

d(Calc.) for γ -phase, using $a = 2.961 \text{ \AA}$, $c = 4.778 \text{ \AA}$

d(Calc.) for $(\alpha' + \alpha)$ phases using $a_0 = 4.144 \text{ \AA}$

Since the reflections from the hexagonal γ -phase contribute to the observed intensities where these reflections nearly coincide with those of the α' -phase, an accurate quantitative comparison of observed and calculated intensities cannot be made.

Four different films, exposed at one hour, two hours, five hours and ten hours respectively were used to obtain the observed intensity values given in Table 8. In this way the weakest reflections were recorded on the ten-hour exposed film but not on the one and two hours films, but the strongest reflections were "overexposed" on the ten-hour film. To obtain the intensity values of the "overexposed" reflections on the ten-hour film the one and two-hour films were used and the intensity values were multiplied by ten and five respectively to correct for the shorter exposure times of these films. The observed intensities were assigned values of 1 to 100 on each film relative to the reflection 10.2. This reflection was chosen because it was within the "readable" intensity range on all films, and could conveniently be assigned a value of 10 on the one-hour film, a value of 100 on the ten-hour film. The observed intensity values are thus all relative to the same basis and are self-consistent. In using a number of films exposed at different times a much larger range of "readable" intensities can be recorded than in using a single film only.

At 165°C and at 76.69 per cent silver the α' -phase still exists (Table 9) but at 325°C this phase does not exist as far as could be determined by x-ray diffraction, but the α -phase does exist as can be seen in the photomicrograph of Plate 8. These observations indicate that the α' -phase is

formed at 187°C by a peritectoid phase-reaction which is in agreement with the phase diagram of Weibke and Eggers (61) although they have not shown this phase-reaction. The homogeneous field of the α' -phase could not be established. Indications are that the composition of the α' -phase is Ag_3In i.e. approximately 73.8 per cent silver. The α and α' phases were not distinguishable microscopically.

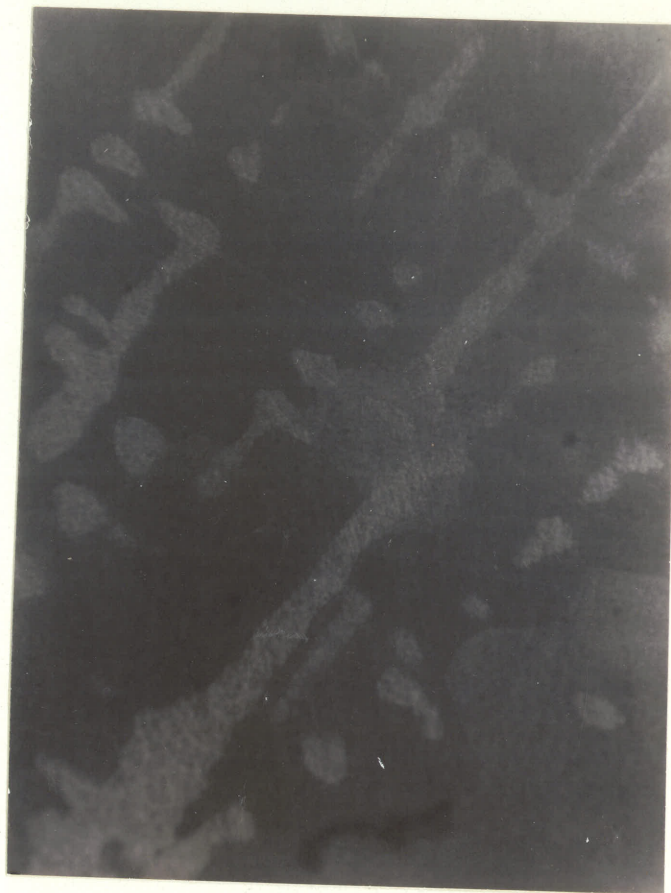


PLATE 8

ALLOY NO. 7 COMPOSITION 76.69% Ag
QUENCHED FROM 325°C.

Magnification Approx. 100X. Alloy
is heterogeneous consisting of ($\alpha + \gamma$)
phases. The lighter phase is α .

TABLE 9

INTERPLANAR SPACINGS (d) OF SILVER-INDIUM ALLOYS

(ANNEALED AT 129°C AND 165°C)

hkl	Alloy No. 14		Alloy No. 11		Alloy No. 17		Alloy No. 12		Alloy No. 18		Alloy No. 13	
α' -Phase	76.69% Ag		76.69% Ag		70.15% Ag		70.15% Ag		68.68% Ag		68.68% Ag	
	$\alpha'+\gamma^*$		$(\alpha'+\gamma)$		$(\gamma+\epsilon)$		(γ)		$(\gamma+\epsilon)$		γ	
	129°C		165°C		129°C		165°C		129°C		165°C	
	I	d(Å)	I	d(Å)	I	d(Å)	I	d(Å)	I	d(Å)	I	d(Å)
100	0.5	4.12										
110	0.5	2.91										
	3	2.543	3	2.544	4	2.556	5	2.570	6	2.556	5	2.580
111	10	2.380	10	2.389	5	2.387	5	2.380	4	2.391	6	2.385
					3	2.326			9	2.325		
	5	2.244	8	2.250	10	2.263	10	2.256	10	2.255	10	2.264
200	6	2.066	0.5	2.085					0.5	2.103		
									0.5	2.023		
120	0.5	1.781							0.5	1.937		
	1	1.740	1	1.746	4	1.749	4	1.746	0.5	1.802		
220	7	1.464	5	1.470					5	1.746	3	1.753
					3	1.481	4	1.484	3	1.645		
									6	1.479	4	1.491
									0.5	1.457		
									1	1.426		
	2	1.352	4	1.355	6	1.354	6	1.353	0.5	1.395		
					0.5	1.344			7	1.354	5	1.354
					5	1.259	6	1.262	7	1.343		
311	8	1.249	6	1.255					6	1.258	4	1.275
	1	1.228	0.5	1.233	2	1.239	3	1.240	3	1.237	3	1.246
					0.5	1.215			3	1.216		
222	4	1.195	2	1.200	1	1.195	1	1.193	2	1.197	1	1.194
					0.5	1.129	0.5	1.133	1	1.165		
									1	1.130	0.5	1.135

Table 9 (Continued)

hkl α' -Phase	Alloy No. 14 76.69% Ag $\alpha'+\gamma^*$ 129°C		Alloy No. 11 76.69% Ag ($\alpha'+\gamma$) 165°C		Alloy No. 17 70.15% Ag ($\gamma+\epsilon$) 129°C		Alloy No. 12 70.15% Ag (γ) 165°C		Alloy No. 18 68.68% Ag ($\gamma+\epsilon$) 129°C		Alloy No. 13 68.68% Ag γ 165°C	
					0.5	1.0826	0.5	1.0829	1	1.0835	1	1.0320
400	1	1.0332							0.5	1.0408		
	1	0.9935	0.5	0.9949	3	0.9979	3	1.0008	4	0.9976	1	1.0030
	4	0.9495	0.5	0.9467	3	0.9492	4	0.9538	0.5	0.9789		
420	5	0.9264	3W	0.9291	4	0.9298	4	0.9312	5	0.9491	3	0.9570
					4	0.8959	3W	0.8973	4	0.9300	3	0.9323
									2	0.9252		
									6	0.8958	3	0.8963
									2	0.8802		
									1	0.8738		
									1	0.8605		
422	3	0.8454							2	0.8541		
	0.5	0.8247	0.5W	0.8260	6	0.8283	4W	0.8315	4W	0.8279		
									2	0.8180		
333	6	0.7978	1W	0.8003	1	0.7976			4	0.8071		
									0.5	0.7865		
									4	0.7766		

* indicates metastable phase.

The γ -Phase and Adjoining Regions

From the x-ray diffraction data of alloys annealed at 129°C, compiled in Table 6, it is evident that all three alloys of composition 76.69; 73.82; 72.11 per cent silver respectively are heterogeneous, and consist of (α' + γ)-phases. The d-values of the pure γ and α' phases, calculated by using the determined cell edges and the appropriate "Miller indices" have been included in this table, for reference.

Since the hexagonal γ -phase has some diffraction lines which very nearly coincide with some of those of the cubic α' -phase, not all diffraction lines belonging to the α' -phase could be assigned unambiguously to this latter phase, but a sufficient number of lines were unambiguously those of the α' -phase and could not be accounted for by pure γ -phase, showing that all three alloys are heterogeneous. The intensities of diffraction lines belonging to the α' -phase are smallest for the 72.11 per cent silver alloy, though the α' -phase still exists in small amounts in this alloy at 129°C. Since the indium-rich boundary of the γ -phase is at approximately 70.3 per cent silver the composition range of the γ -phase at room temperature must be less than 1.8 per cent. On the basis of the intensity data in Table 6, the silver-rich boundary of the γ -phase is crudely estimated to lie at 71.0 per cent silver, which means that the composition range of the γ -phase is less than one per cent at room temperature. At 325°C, the 76.69 per cent silver alloy (Alloy No. 7), contained α -phase which was identified by x-ray microanalysis (Plate 8), but contained no α' -phase. An Alloy of composition 72.11 per cent silver (Alloy No. 8), did not contain α -phase or

α' -phase at 325°C , but γ -phase. Neither were the two phases present at higher temperatures in the latter two alloys, as was ascertained by high-temperature x-ray diffraction. These observations are in agreement with those of previous investigations (61,29) and extension of the high temperature phase boundary of the γ -phase on the silver-rich side to a temperature of 187°C is essentially correct, as established previously.

Referring to Table 9, it is seen that alloys of composition 70.15 and 68.68 per cent silver, respectively, are both heterogeneous at 129°C , and consist of ($\epsilon + \gamma$)-phases, but both are homogeneous (γ) at 165°C . High-temperature x-ray diffraction in the range 300 to 550°C showed that these alloys remained single-phased (γ) at these higher temperatures. The transition from ϵ to γ was observed by high-temperature x-ray diffraction for alloys of composition 66.50 and 65.28 per cent silver respectively. At 250°C only the pure ϵ -spectrum was observed and at 350° only the pure γ -spectrum was observed.

Hellner (29) found that an alloy of composition Ag_3In (73.82% Ag) was homogeneous (γ) at room temperature. In my investigation an alloy of this composition was found to be heterogeneous at "room temperature" (129°C) and consisted of ($\gamma + \alpha'$) while at 165°C the same alloy was homogeneous (γ), and this structure was retained at room temperature if the alloy was annealed for only one week at 129°C . Three weeks of annealing at this temperature gave a heterogeneous alloy ($\alpha' + \gamma$) (Table 6). Hellner's (29) observation is readily explained if one considers that he annealed this alloy for one week at 150°C which is probably too high a temperature and the annealing time is too short,



PLATE 9

ALLOY NO. 14 COMPOSITION 76.69% Ag
ANNEALED 21 DAYS AT 129°C.

Magnification approx. 100X. Showing
presence of γ -phase, α' -phase and pro-
bably also α -phase. The α and α' phases
were not distinguishable microscopically.

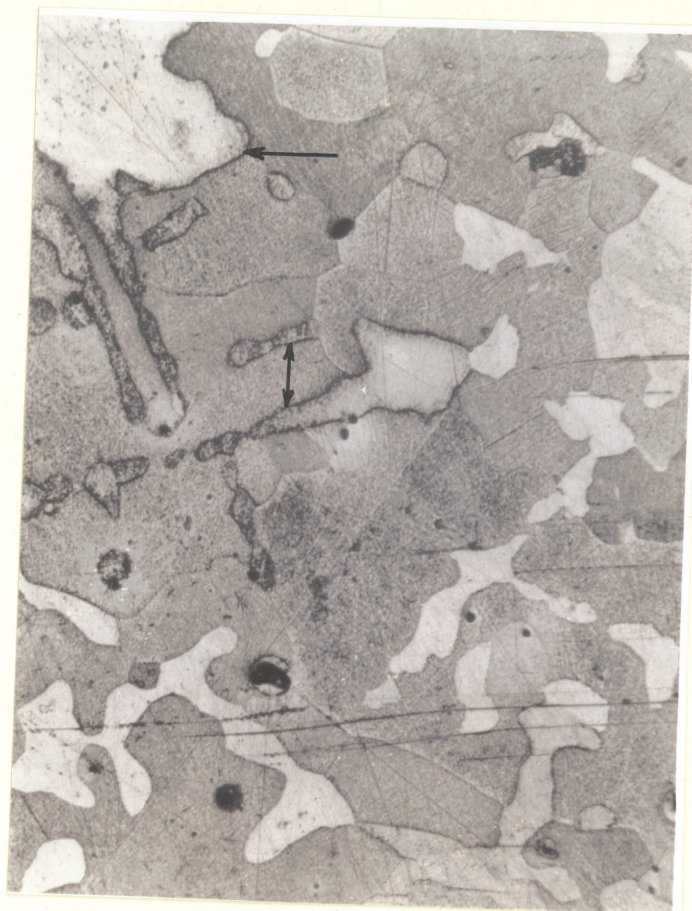


PLATE 10

ALLOY NO. 14 COMPOSITION 76.69% Ag
Annealed 21 Days at 129°C and two
months at room temperature. Magnifi-
cation approx. 100X. γ -phase reacting
at grain boundaries.

for equilibrium phases to form.

The symbol " γ^* " in Tables 6 and 9, indicates that the γ -phase is not an equilibrium phase, at room temperature at an overall composition of 76.69 per cent silver, though some γ -phase is retained even after three weeks of annealing at 129°C. The observed α' -phase probably consists of ($\alpha + \alpha'$) phases, but α -phase cannot be differentiated from α' -phase by x-ray powder-diffraction, if the latter phase (α') is present.

That the γ -phase is not stable at the overall composition of 76.69 per cent silver at room temperature can be seen by comparing the two photomicrographs, (Plates 9 and 10) of this alloy. Plate 9 is a photomicrograph of the alloy after annealing for three weeks at 129°C. Plate 10 is a photomicrograph of the same alloy (and same annealing treatment) but taken two months later (at room temperature), showing that the γ -phase is slowly transforming, particularly at the grain boundaries, presumably to ($\alpha + \alpha'$). The newly formed phase did not present a sufficiently large area to be analyzed by either electron probe or the x-ray micro technique.

At 325°C, the γ -phase has a very wide range of homogeneity. The present investigation showed that the indium-rich phase boundary of the γ -phase (above 300°C) is at a higher indium concentration than that given by Weibke and Eggers. For example, at 325°C, as estimated from the phase diagram of the above authors, it lies at 66.3 per cent silver compared with 52.5 per cent silver at the same temperature found in my investigation. The high-temperature γ -phase boundary was established by differential thermal analysis and x-ray diffraction.

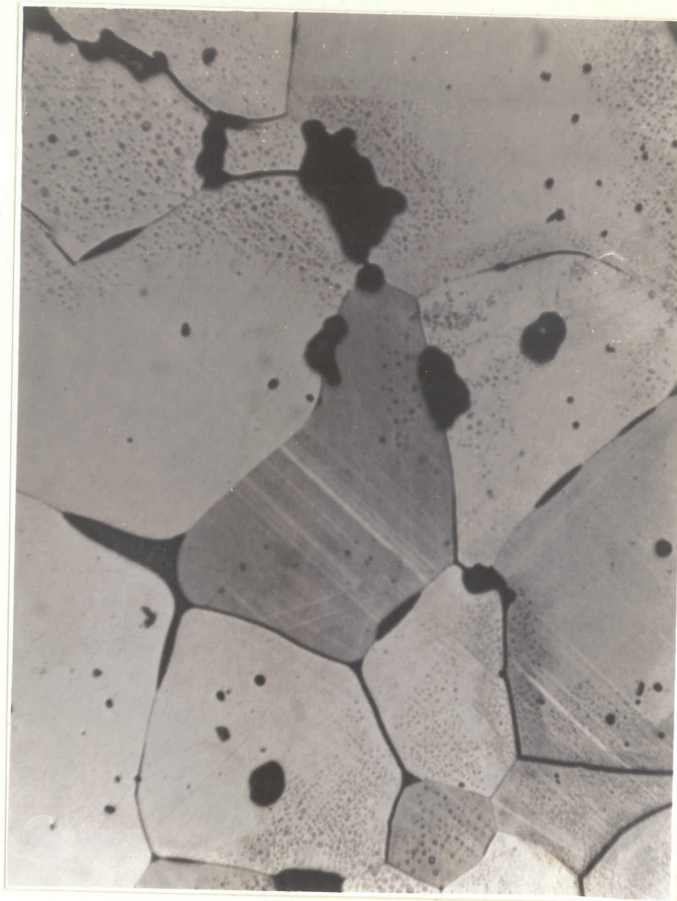


PLATE 11

ALLOY NO. 28 COMPOSITION 62.85% Ag
Quenched from 275°C

Magnification approx. 100X. The dark lines between grains and the dark areas at the corners of grains are the indium-rich soft phase. The irregular or round dark areas are holes in the grains. The grains are γ -phase.

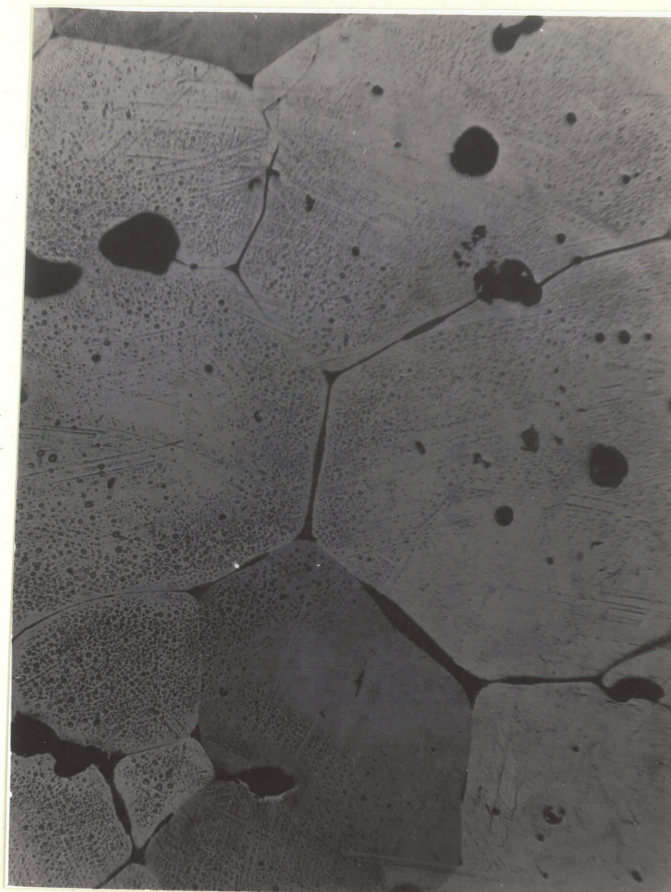


PLATE 12

ALLOY NO. 29 COMPOSITION 55.63% Ag
Quenched from 325°C

Magnification approx. 100X. Intergrain
liquefaction is evident. Dark lines be-
tween grains are due to solidified In-
phase produced by metatectic reaction.
The grains are γ -phase.

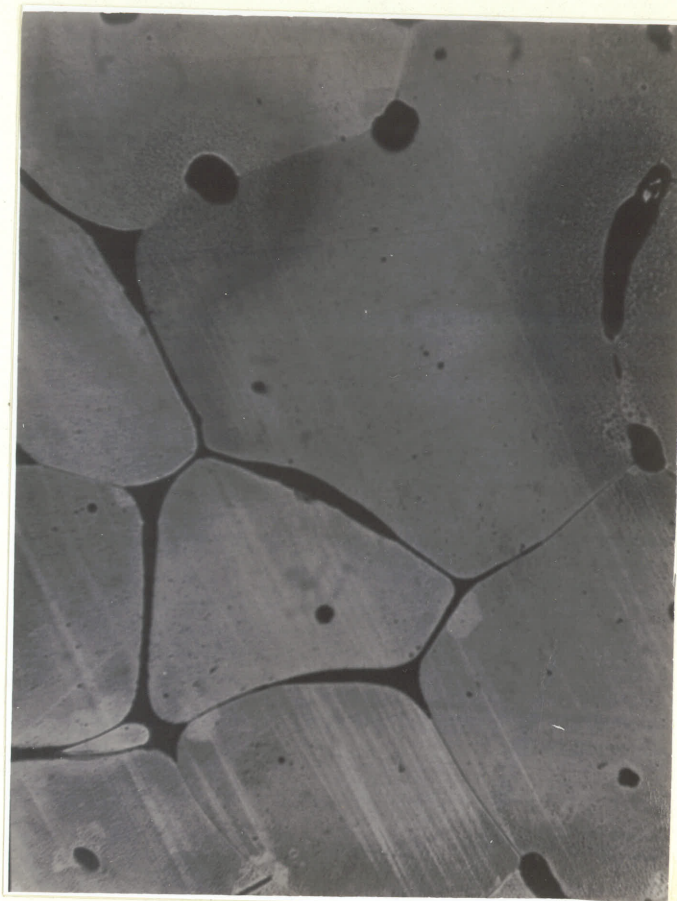


PLATE 13

ALLOY NO. 30 COMPOSITION 55.63% Ag
Quenched from 275°C

Magnification approx. 100X. Intergrain
liquefaction due to metatectic reaction
is evident. Grains are γ -phase (light
areas).

The phase diagram, Figs. 13, 14 is the result of my investigation.

The γ -phase undergoes a metatectic decomposition at 205°C in a composition range of 65.0 to 52.5 per cent silver. Alloys of compositions within that range which were quenched from temperatures above 205°C show intergrain liquefaction, as can be seen in Plates 11, 12, 13. The dark lines between grains and the triangular areas at the grain junctures could be clearly distinguished under the microscope as a second phase which was very soft - almost pure indium. The round and irregular areas (dark) within the grains in these photomicrographs are holes.

When an alloy of such a composition is quenched from temperatures higher than 205°C some melting will take place because of the "metatectic" reaction at 205°C . During the relatively short time required to traverse the temperature interval of 205°C to 166°C when the alloy is quenched in liquid nitrogen, only a small amount of liquid can be expected to form since melting is hardly an instantaneous process. Melting in this case occurs first at the grain boundaries as in normal melting, as can be seen from Plates 11, 12, 13. As far as could be ascertained the formation of the ϕ -phase does not occur under these drastic conditions and the liquid remains as such below 166°C until it freezes to the indium-rich intergrain-phase seen in these photomicrographs.

Two alloys of composition 55.63 and 62.85 per cent silver were examined by quenching from 325°C and 275°C . Photomicrographs of these quenched alloys are shown in Plates 12, 11, 13. Except for intergrain liquefaction the alloys are unmistakably homogeneous. X-ray diffraction

TABLE 10

INTERPLANAR SPACINGS (d) OF SILVER-INDIUM ALLOYS

(ANNEALED AT VARIOUS TEMPERATURES)

hkl ϕ-Phase	Alloy No. 24 34.00% Ag ϕ-Phase 135°C	Alloy No. 32 55.63% Ag (ϵ+ϕ) 135°C	Alloy No. 19 66.50% Ag ϵ-Phase 129°C	Alloy No. 31 55.63% Ag (ϵ+γ) 225°C	Alloy No. 29 55.63% Ag γ-Phase 325°C	hkl γ-Phase			
I	d(Å)	I	d(Å)	I	d(Å)	I	d(Å)		
222	0.5	2.83	0.5	2.85	1	2.84			
	10	2.695	1	2.692					
321			1	2.634	1	2.632			
	5	2.429	0.5	2.425			1	2.569	10.0
411			10	2.331	10	2.323	8	2.297	00.2
	8	2.172	1	2.172			8	2.254	10.1
332			1	2.105	1	2.097			
422			0.5	2.018	0.5	2.010			
510			1	1.942	1	1.933			
521			0.5	1.808	0.5	1.800			
600			4	1.650	3	1.645	2	1.740	10.2
	5	1.597	0.5	1.598	0.5	1.601	2	1.631	
	1	1.536							
	3	1.466	0.5	1.463			2	1.492	11.0
631							2	1.503	11.0
444			1	1.431	1	1.457	0.5	1.448	
710	5	1.402	1	1.398	2	1.425	0.5	1.418	
721			1	1.395	1	1.395	0.5	1.388	
			8	1.349	8	1.344	7	1.336	10.3
							4	1.266	20.0
							6	1.368	
							5	1.273	

Table 10 (Continued)

hkl ϕ-Phase	Alloy No. 24 24.00% Ag ϕ-Phase 135°C	Alloy No. 32 55.63% Ag (ϕ+δ) 135°C	Alloy No. 19 66.50% Ag ϕ-Phase 129°C	Alloy No. 31 55.63% Ag (ϕ+γ) 225°C	Alloy No. 29 55.63% Ag γ-Phase 325°C	hkl γ-Phase
732			0.5 1.254	3 1.251	2 1.254	11.2
811	2 1.244 2 1.214 3 1.178	5 1.210	6 1.217	4 1.210		
822		1 1.167	3 1.165	0.5 1.161		
662		0.5 1.134	1 1.133			
930	4 1.0540	2 1.0430	2 1.0415			
941		3 0.9986	3 0.9976	0.5 1.0073	1 1.0108	20.3
10·1·1		3 0.9791	3 0.9812	0.5 0.9963		
10·2·2		1 0.9516	1 0.9505	0.5 0.9645	2 0.9677	21.0
871	1 0.9321			1 0.9351	3 0.9392	11.4
	3 0.9209	4 0.9266	4 0.9259	2 0.9258		
	4 0.9035	3 0.9037				
10·4·2			1 0.9023	0.5 0.9028	3 0.9007	21.2
11·2·1	1 0.8881	5 0.8817	5 0.8809	4 0.8817		
880		0.5 0.8752	0.5 0.8739			
10·4·4		3 0.8617	2 0.8609	0.5 0.8612		
11·3·2		3 0.8552	2 0.8593	0.5 0.8551		
	2 0.8441					
965		0.5 0.8312	0.5 0.8302	2 0.8400	2 0.8421	30.1
	3 0.8225					
12·1·1		4 0.8194	3 0.8186	3 0.8204		
	3 0.8110					
11·5·2		6 0.8086	5 0.8078	4 0.8101		
	0.5 0.7998					
11·6·1		4 0.7870	2 0.7871			
12·3·3	7 0.7766	5 0.7780	4 0.7772	2 0.7803		

(micro analysis) for the alloy of 55.63 per cent silver, given in Table 10, shows that the phase in question is the hexagonal γ -phase. High-temperature x-ray diffraction showed that this alloy does not undergo any change in the temperature range of investigation viz. 325°C to 555°C , but remains homogeneous. The same alloy was heterogeneous at 225°C , (Table 10), consisting of $(\gamma + \epsilon)$ phases. Since the latter alloy (55.63% Ag) is γ -phase at 325°C , but is heterogeneous, consisting of $(\gamma + \epsilon)$ phases, at 225°C (Table 10) the γ -phase boundary i.e. $\gamma/(\gamma + \epsilon)$ must obviously lie in this temperature range. Furthermore, since this alloy consists of γ -phase at 325°C , the γ -phase solidus must obviously lie at a concentration less than 55.63 per cent silver at this temperature. These findings, together with differential thermal analysis data, were used to draw the $\gamma/(\gamma + \epsilon)$ boundary and the γ -solidus in the phase diagram Fig. 14. The γ -solidus now established by me is displaced to much lower silver concentrations, particularly at the lower temperatures, when compared with the solidus given by Weibke and Eggers (61). For example, the solidus at 325°C lies at 66.3 per cent silver according to the phase diagram of Weibke and Eggers, Fig. 1, compared to 52.5 per cent silver found in my investigation, at the same temperature.

In Table 10, the d-values of β -phase, the γ -phase, and the corresponding Miller indices, are included for reference.

The diffraction lines of the hexagonal γ -phase were indexed and the best lattice parameters were determined in the following way:

For a hexagonal system

$$\frac{1}{d_{hkl}^2} = \frac{4}{3} \frac{(h^2 + hk + k^2)}{a^2} + \frac{1}{c^2} \quad (1)$$

$$\text{or} \quad \frac{1}{d^2} = \frac{4}{3} \frac{N_H}{a^2} + \frac{1}{c^2} \quad (2)$$

where $N_H = (h^2 + hk + k^2)$. Using initially the lattice parameters given by Goldschmidt (24) $a = 2.950$, $c = 4.769$, a number of N_H -values were calculated for each d -value for a range of assigned l -integers, from the above equation. For example, l was assigned values of $l = 0, 1, 2, \dots, 6$ in the front-reflection region and seven different N_H values were calculated for each d -value. Since N_H must be an integer the N_H -value closest to a permissible integer was the desired value. The particular l -value used in calculating the "correct" N_H -value was the proper l -index. By using the tables of Azaroff and Buerger (50) the h and k indices were easily and conveniently found once N_H was known. In this fashion the correct hkl indices were established for each d -value. Since the computations are tedious and time consuming a program was written for a small computer ("Programma 101") which calculated a series of N_H -values for each given d -value, beginning with $l = 0$ and reiterating the calculation after increasing l by one, until the limit imposed on l was reached. Writing equation (2) for two different d -values (dropping the "H" on N_H):

$$\frac{1}{d_1^2} = \frac{4}{3} \frac{N_1}{a^2} + \frac{1}{c^2} \quad \text{when } d_1 \text{ and } d_2 \text{ are two different } d\text{-values}$$

$$\frac{1}{d_2^2} = \frac{4}{3} \frac{N_2}{a^2} + \frac{1}{c^2} \quad \text{and } N_1, l_1; \text{ and } N_2, l_2; \text{ are the respective}$$

indices, the two equations can be solved for a and c simultaneously giving:

$$a = \frac{4 (l_1^2 N_2 - l_2^2 N_1)^{1/2}}{3 \left[\frac{l_1^2}{d_2^2} - \frac{l_2^2}{d_1^2} \right]^{1/2}}$$

$$c = \frac{(N_1 l_2^2 - N_2 l_1^2)^{1/2}}{\left[\frac{N_1}{d_2^2} - \frac{N_2}{d_1^2} \right]^{1/2}}$$

Successive pairs of d -values (and their corresponding Miller indices) were used to calculate a number of " a " and " c " values. The average " a " and " c " values were then obtained and these are the values used in calculating the d -values in Tables 4 and 6.

$$a = 2.961 \pm 0.002 \text{ \AA}^0$$

$$c = 4.778 \pm 0.004 \text{ \AA}^0 \quad \text{at room temperature}$$

The error shown is the mean deviation.

The given cell edges were calculated from the powder diffraction pattern of alloy No. 17 of composition 70.15 per cent silver. Using the d -values in the range $2.263 \geq d \geq 0.9298 \text{ \AA}$ (Table 9). The alloy contained some ϵ -phase. Only the lines belonging to the γ -phase were used. Since the alloy is heterogeneous, the calculated cell edges are valid for the composition at the indium-rich phase-boundary of the γ -phase viz. 70.3 per cent silver. Since the γ -phase has a very small composition range at room temperature (less than one per cent) the lattice edges would be expected to

be very nearly the same at the composition of the silver-rich and the indium-rich phase-boundaries of the γ -phase. The cell-edges of the γ -phase should thus be very nearly the same at any composition i.e. an alloy of any overall composition which is at equilibrium should yield very nearly the same cell edges. Only if the γ -phase was not at equilibrium at room temperature would substantial changes in cell edges with a change in composition (at room temperature) be expected. The cell edges determined by Goldschmidt (24), Hellner (29) and myself are given below for comparison.

Goldschmidt (24)	$a = 2.950 \pm .003 \text{ kX} = 2.956 \text{ \AA}$	at Ag_3In (room temperature)
	$c = 4.769 \pm .005 \text{ kX} = 4.779 \text{ \AA}$	
Hellner (29)	$a = 2.983 \text{ \AA}$	at $\text{Ag}_{68}\text{In}_{32}$ (room temperature)
	$c = 4.789 \text{ \AA}$	
Present Investigation	$a = 2.961 \pm .002 \text{ \AA}$	at 70.3 per cent silver (room temperature)
	$c = 4.778 \pm .004 \text{ \AA}$	

The substantial difference in cell edges as determined by Goldschmidt (24) and Hellner (29) compared with my values suggests that prior investigators did not anneal the alloys at a sufficiently low temperature. This conclusion is also supported by the fact that I found an alloy 73.82 per cent silver (Table 6) to be heterogeneous consisting of ($\gamma + \alpha'$) phases at room temperature while Hellner (29) found the same alloy to be homogeneous (γ).

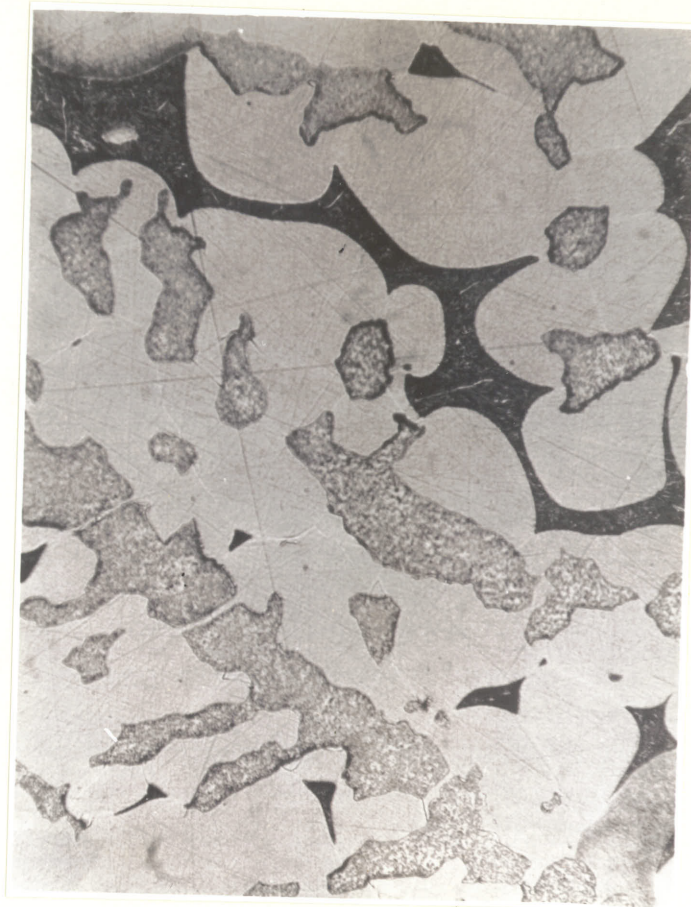


PLATE 14

PHOTOMICROGRAPH OF
ALLOY NO. 24, COMPOSITION 34.00% Ag
Annealed two weeks at 135°C

Magnification approx. 100X. Metastable
γ-phase (speckled islands) within the δ-
phase (bright) can be seen. The black
area is In-Phase.

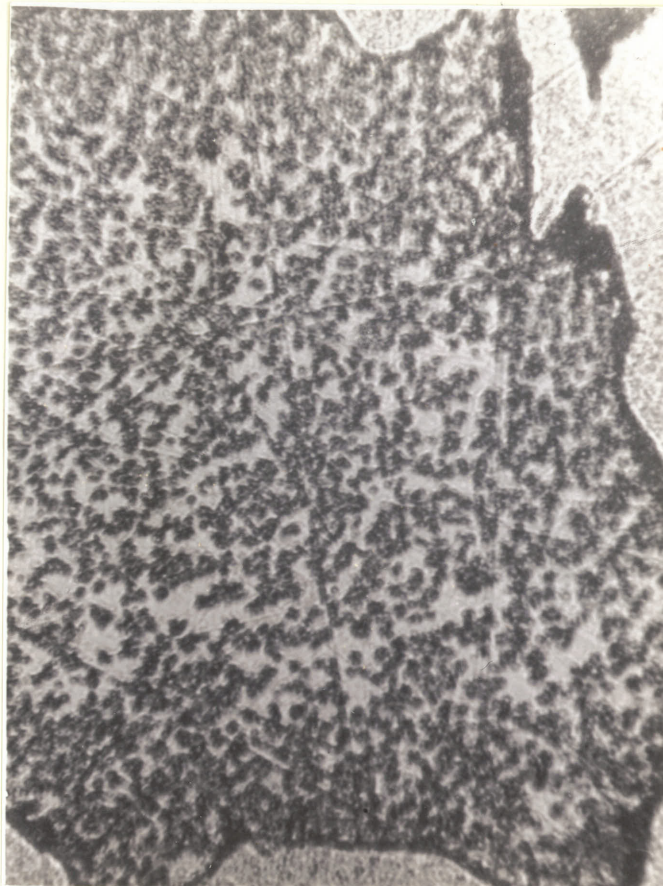


PLATE 15

ALLOY NO. 24, COMPOSITION 34.00% Ag
Magnification approx. 800X. The "is-
lands" of γ -phase shown in plate 14 are
shown magnified.

Metastable States

The γ -phase exists metastably at room temperature (at compositions where it should not exist) even after prolonged annealing at 135°C , as shown in Plate 14, where the gray "islands" are the γ -phase. A comparison with Plate 2 which is a photomicrograph of the same alloy, which was not annealed and was subjected to differential thermal analysis only, shows that the narrow "rim" of ϕ -phase (in the latter plate) surrounding the large "islands" of γ -phase has grown considerably after annealing, while the area of the γ -phase has diminished. The "islands" of γ -phase in Plate 14 have a speckled appearance which is clearly revealed in the enlarged photomicrograph of Plate 15.

New phases are apparently being precipitated within the metastable γ -phase. The individual grains of the precipitate are at this stage too small to be identified by electron probe microanalysis or any other means. The precipitate is probably ϵ -phase and an indium-rich phase resulting from the related occurrence of the metatectic phase reaction which normally takes place at 205°C . The indium-rich phase is itself metastable at this composition, viz., 34.00 per cent silver, and it should then react with the remaining γ -phase to form ϕ -phase. X-ray diffraction data of the end-products of this phase-reaction, which support this view, were obtained. An alloy of composition 33.89 per cent silver was annealed for four weeks at 135°C and allowed to remain at room temperature for two months in a polished state before the photograph was taken which is shown in Plate 16. The areas where the γ -phase previously existed as "islands" are clearly outlined.

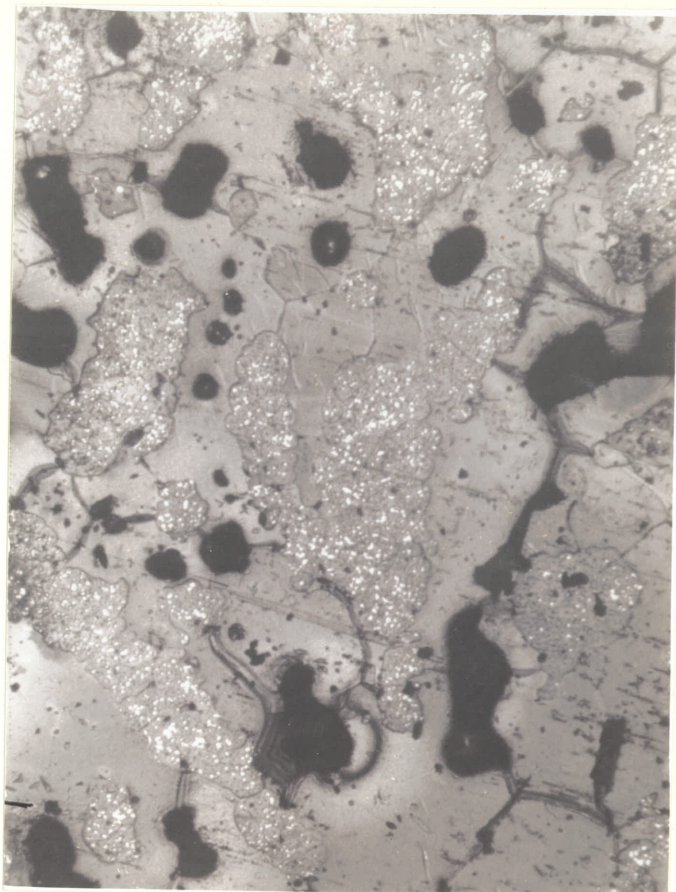


PLATE 16

ALLOY NO. 26, COMPOSITION 33.89% Ag

Magnification approx. 100X. Annealed four weeks at 135°C. Within areas previously occupied by metastable γ -phase, a small amount of ϵ -phase (light areas) has formed. Black areas are holes. The major constituent is ϕ -phase.

Within these areas another phase, occurring as small bright areas, is evident. X-ray diffraction of the heterogeneous areas (micro technique) showed that the phases are ($\epsilon + \phi$).

The sequence of events taking place during the attainment of equilibrium in alloys with less than 52.5 per cent silver (for example the 34.00 per cent silver alloy) must be as follows: From the molten alloy the γ -phase is precipitated first as a solid at the temperature of the γ -solidus. At 205°C the metatectic reaction occurs and the solid remelts partially. At 166°C an additional solid phase is precipitated - the ϕ -phase. The latter phase nucleates preferentially on the γ -phase forming eventually a visible "rim" or shell around the γ -phase as in Plate 2. Since the ϕ -phase has a composition intermediate between γ -phase and the indium-rich phase, further growth of the ϕ -phase must involve diffusion of silver and indium through the latter phase, and consequently growth becomes slower with time as the total thickness of ϕ -phase through which diffusion must proceed becomes larger. Simultaneously the metatectic reaction may proceed slowly throughout the γ -phase yielding ultimately ϕ -phase plus ϵ -phase. The latter process may become the predominant process, with time, whereby the alloy reaches the equilibrium state. Both processes are understandably slow; γ -phase is thus retained metastably unless the alloy is annealed for a long time.

The non-equilibrium states described, which prevail during differential analysis, will have the effect of extending the 144°C-isotherm to a much higher silver concentration than would be observed under equilibrium conditions. This is shown in the photomicrograph of Plate 1.

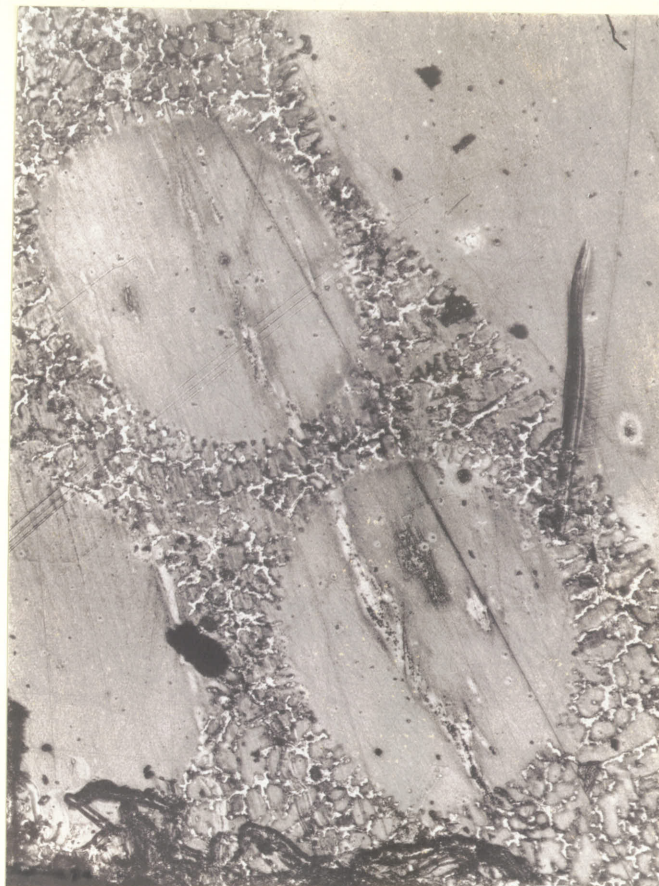


PLATE 17

ALLOY NO. 3, COMPOSITION 68.68% Ag

Quenched from 655°C. Magnification approx. 100X. Grains of γ -phase (light) partially transformed to ($\gamma + \epsilon$) phases.

The γ -phase is also retained metastably at room temperature at compositions lying between the α -phase boundary and 71.0 per cent silver, and the ϵ -phase boundary and 70.3 per cent silver, unless the alloy is properly annealed. Transformation to the equilibrium phases can however be induced by thermal shock it seems. Plate 17 is a photomicrograph of an alloy of composition 68.68 per cent silver which was quenched from 655°C in liquid nitrogen. X-ray diffraction (micro analysis) showed that the homogeneous (bright) areas are grains of γ -phase while the heterogeneous area between the grains consists of $(\gamma + \epsilon)$ phases. The same alloy quenched from 500°C did not undergo this transformation, but remained homogeneous throughout. Similarly the 72.11 per cent silver alloy (Alloy Nos. 2, 5) when quenched from either 655°C or 500°C did not undergo the transformation to $(\gamma + \epsilon)$. This was not surprising since the latter composition does not fall within the $(\gamma + \epsilon)$ region at any temperature. It is probable that the alloy of 68.68 per cent silver was in the γ + liquid field at 655°C prior to quenching - judging from the appearance of Plate 17, and that the liquid transformed to the ϵ -phase after quenching. But if this did indeed happen, it is not clear why the liquid should not have transformed to the γ -phase after quenching as would be expected.

Alloys of metastable γ -phase, which have an overall composition that falls within the $(\phi + \epsilon)$ range at room temperature, can be readily transformed to the equilibrium phases $(\phi + \epsilon)$ by filing. The filings so produced, consist of $(\phi + \epsilon)$ phases. It was for this reason that quenched alloys had to be analyzed using the microtechnique of x-ray diffraction, which did not cause a transformation to the equilibrium phases to take place.

The ϕ -Phase and Adjoining Regions

To ascertain whether the indium-phase which is present at room temperature in alloys of composition lying between the ϵ -phase and AgIn_2 is in fact present metastably, an alloy of 36.04 per cent silver was annealed at 135°C for four weeks. Microscopic examination, as shown in Plate 18, showed that no indium-phase was present, and that the alloy consisted of only two phases - largely ϕ -phase and some ϵ -phase (bright areas). Thus, given sufficient time, the indium-phase disappears at temperatures lower than 166°C , in the composition range in question, and this means that any indium-phase present at room temperature in such alloys is present metastably.

Attempts were made to define the composition of the ϕ -phase more closely. An alloy 33.89 per cent silver was also annealed at 135°C for four weeks to establish equilibrium. It still contained a small amount of ϵ -phase as shown in Plate 16. Similarly, an alloy of 31.97 per cent silver (AgIn_2) was annealed for four weeks at 135°C . As shown in Plate 19, three phases are still present; hence this alloy has not reached equilibrium. The few small bright areas were identified by x-ray diffraction as γ -phase. The major constituent is ϕ -phase. The dark gray areas are indium-phase. From the observation that the indium-phase presented a larger total area than the γ -phase it was concluded that the equilibrium alloy would be heterogeneous, consisting mainly of ϕ -phase and a very small amount of indium-phase. The composition of the ϕ -phase thus lies between 31.97 per cent silver and 33.89 per cent silver. It is estimated that the composition



PLATE 18

ALLOY NO. 25, COMPOSITION 36.04% Ag

Annealed four weeks at 135°C. Magnification approx. 100X. Small amount of ϵ -phase (light areas) is present within the ϕ -phase.

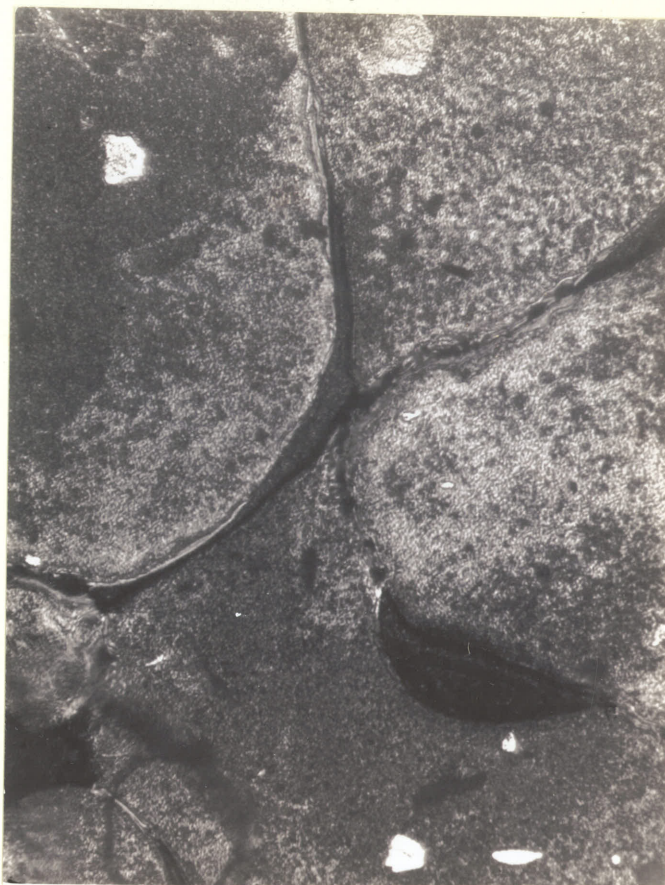


PLATE 19

ALLOY NO. 27, COMPOSITION 31.97% Ag

Annealed four weeks at 135°C. Magnification approx. 100X. A small amount of metastable γ -phase (light areas) is present as well as In-phase, (black areas). Major constituent is δ -phase.

TABLE 11

COMPARISON OF MEASURED d-VALUES($\text{\AA}$) OF HELLNER (29)

AND THIS INVESTIGATION WITH CALCULATED VALUES

Hellner (obs.)	Alloy No. 24 Composition 34.00% Ag	Calculated**	hkl
d ($\text{\AA}$) ϕ	d(obs.)* $\text{\AA}$ ϕ	d $\text{\AA}$ ϕ	
I	I		
	1/2 2.83	2.802	002
3 $\frac{1}{2}$ 2.694	10 2.695	2.6937	211
2 $\frac{1}{2}$ 2.430	5 2.429	2.4286	220
		2.4271	112
3+ 2.173	8 2.172	2.1722	310
		2.1711	202
4- 1.597	5 1.597	1.5969	411
		1.5961	213
2- 1.534	1 1.536	1.5360	420
3 $\frac{1}{2}$ 1.464	3 1.466	1.4642	402
4 $\frac{1}{2}$ 1.402	5 1.402	1.4018	332
		1.4010	004
1 1.348		1.3471	510
		1.3469	422
$\frac{1}{2}$ 1.335		1.3461	114
		1.3343	431
		1.3338	323
$\frac{1}{2}$ 1.244	2 1.244	1.2972	204
		1.2437	521
		1.2433	413
		1.2143	440
4 1.215	2 1.214	1.2141	512
		1.2135	224
5+ 1.178	3 1.178	1.1774	314
	4 1.054	1.0534	523
	1 1.0344	1.0351	424
	1 0.9321	0.9303	543
		0.9299	415
	3 0.9209	0.9215	335
	4 0.9035	0.9019	730, 642
	1 0.8881	0.8865	604
	2 0.8441	0.8423	811, 741
	3 0.8225	0.8236	445
	3 0.8110	0.8120	535
	1/2 0.7998	0.8009	605
	7 0.7766	0.7752	743

* This work, x-ray microanalysis

** using $a = 6.869 \text{ \AA}$, $c = 5.604 \text{ \AA}$

of the ϕ -phase is a few tenths of a per cent higher in silver than AgIn_2 . The homogeneous range of the ϕ -phase is definitely less than two per cent. This estimate is based on the observation, under the microscope, that the amount of In-phase present in the 31.97% silver alloy is very small.

The Miller indices of the powder diffraction lines of the tetragonal ϕ -phase and the cell dimensions were determined by Hellner (29). The latter are given as $a = 6.869 \pm .005 \text{ \AA}$; $c = 5.604 \pm .005 \text{ \AA}$; with four atoms per unit cell.

In Table 11, d-values measured by Hellner (29) and those measured by me are given, together with the calculated d-values, using the cell edges and Miller indices given by Hellner (29). The calculated and measured values are in good agreement. No improvement in the dimensions of the cell edges over those given by Hellner could be attained with the present data.

Summary

At high temperatures the liquidus was found to lie approximately 8°C higher than that determined by Weibke and Eggers (61). At lower temperatures the agreement is good.

The isothermal phase transformation at 287°C claimed by Weibke and Eggers (61) does not exist.

Metastability is a persistent phenomenon in this system. The γ -phase and the indium-phase are retained metastably at room temperature.

The boundaries of the intermediate phases have been redetermined. The γ -phase has a concentration range of 71.0 to 70.3 per cent silver at room temperature. At the composition Ag_3In the alloy of 73.89% Ag is definitely not homogeneous as previously claimed (29). It consists of ($\gamma + \alpha'$) phases. The cell edges of the hexagonal γ -phase were determined as

$$\begin{array}{ll} a = 2.961 \pm 0.002 \text{ \AA} & \\ c = 4.778 \pm 0.004 \text{ \AA} & \end{array} \quad \begin{array}{l} \text{O} \\ \text{A} \end{array} \quad \begin{array}{l} \text{at room temperature} \end{array}$$

The cell edges of the γ -phase determined by Goldschmidt (24) and Hellner (29) were determined most probably for alloys which were not at equilibrium at room temperature. The γ -solidus extends to higher indium concentrations than given by Weibke and Eggers, e.g. at 325°C the γ -solidus is at 52.5 per cent silver according to me, but at 66.3 per cent silver according to Weibke and Eggers (61). The order-disorder transformation of the γ -phase postulated by Hellner (29) does not exist. The γ -phase undergoes a "metatectic" phase-reaction at 205°C which was not known previously.

The ϵ -phase has a concentration range of 67.5 to 65.0 per cent

silver at room temperature. At these compositions the cell edges of the cubic ϵ -phase were determined to be $9.878 \pm 0.004 \text{ \AA}$ and

$$9.887 \pm 0.004 \text{ \AA} \text{ respectively.}$$

The composition range of the ϵ -phase is in reasonably good agreement as determined by Weibke and Egger (61), but obviously the claim (29) that the ϵ -phase is represented by Ag_2In is not correct. The $\gamma/(\gamma + \epsilon)$ boundary was investigated. On the silver-side of ϵ , the $\gamma/(\gamma + \epsilon)$ boundary determined by me is in reasonably good agreement with that established by Hellner (29). On the indium side of ϵ , this boundary was not established previously. The order-disorder transformation of the ϵ -phase claimed by Weibke and Eggers (61) does not exist. The heat effects upon which this claim rests were shown to be due to the $\gamma \rightarrow \epsilon$ transformation.

A new phase α' is claimed to exist at approximately 73.8 per cent silver below 187°C , which is formed by a peritectoid phase reaction at 187°C . It is an ordered version of the α -solid solution with the same cell edge as the latter phase. In the α' -phase the silver atoms occupy the face-centre positions and the indium atoms occupy the corner positions of the cube, yielding a primitive cubic lattice. The cell edge of the α' -phase was found to be $4.144 \pm 0.004 \text{ \AA}$ at room temperature. The justification for this phase is the occurrence of diffraction lines not allowed by the face-centred lattice of the α -phase. A crystal structure was postulated for the α' -phase and intensities of diffraction lines were calculated which were

qualitatively in agreement with the observed intensities.

Attempts were made to define the composition of the ϕ -phase more closely. The composition of the ϕ -phase lies between 31.97 and 33.89 per cent silver. Indications are that the ϕ -phase does not have a composition Ag_2In at room temperature but that it is a few tenths of a per cent higher in silver.

A new phase diagram of the system indium-silver was constructed, and is given in Figs. 13, 14.

THE TERNARY SYSTEM, Ag-In-Al

RESULTS AND DISCUSSION

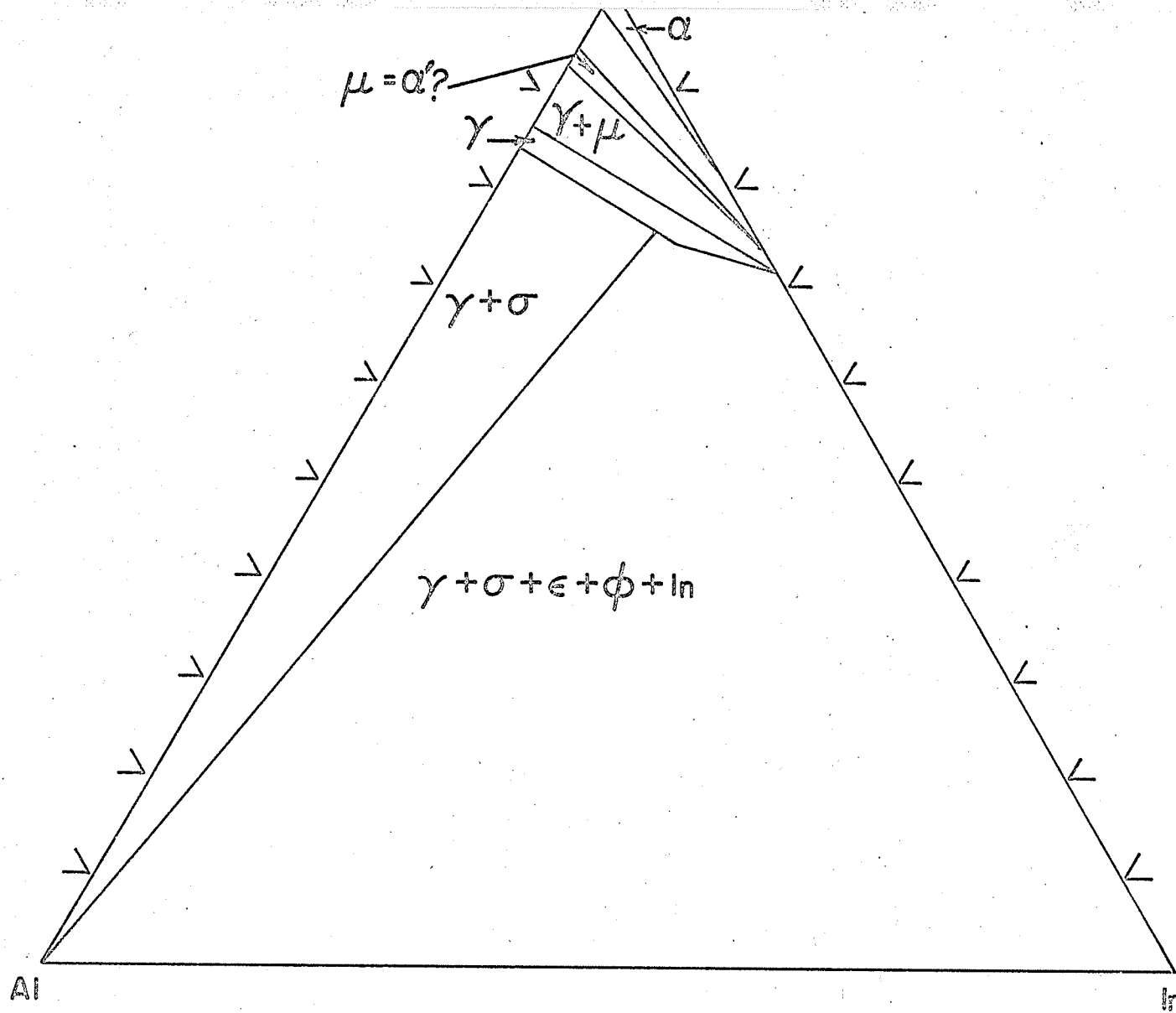


Fig. 20. Section, Showing Area of Metastable Phase Formation (Not an Equilibrium Diagram).

Metastable States

I have established that in the binary system, Ag-In, the γ -phase and the indium phase are retained metastably at room temperature in the concentration region of the 166°C - peritectic reaction, even after prolonged heating. In the ternary system, the same problem occurs. Due to metastability the 143°C - isotherm in "Vertical Section I" of Fig. 17 (p. 169) is longer than it would be at equilibrium. This isotherm, when projected on the basal plane, (room temperature section) defines an area of metastability which is touched by the single-phase regions of the γ , ϵ , ϕ , In and σ phases as shown in Fig. 20. The meaning of this plane is as follows: An alloy of any composition within this area when cooled from the molten state to room temperature will normally consist of the five phases mentioned, or a combination of four of these. The phases that should be present at equilibrium in such an alloy can be obtained from the equilibrium isothermal section in Fig. 21.

Although metastability was a problem within the composition area outlined in Fig. 20, it was possible to deduce which phase was present metastably in an annealed alloy. If for example the four phases $\sigma + \epsilon + \phi + \text{In}$ were obtained at room temperature after annealing, clearly only three phases at most could be equilibrium phases. Since ($\epsilon + \text{In}$) cannot coexist as equilibrium phases at room temperature then the three equilibrium phases could be either ($\sigma + \phi + \text{In}$) or ($\sigma + \phi + \epsilon$). If to a first approximation the composition of the binary ϕ -phase is used as one vertex of the triangle, then one can determine whether In-phase could possibly be obtained for the

given overall composition, since the overall composition would then have to fall within the triangle Al- ϕ -In. If the overall composition does not fall within this triangle, and if the amount of In-phase present in the actual alloy is small relative to the other phases, then one can safely assume that the possible equilibrium phases are $(\sigma + \phi + \epsilon)$ and not $(\sigma + \phi + \text{In})$.



PLATE 20

ALLOY No. 8, COMPOSITION 80.00% Ag,
20.00% Al.

Annealed at 135°C for three weeks.
Grains of ζ-phase separated by the
eutectic matrix. Magnification approx.
80 X



PLATE 21

ALLOY No. 6, COMPOSITION 60.00% Ag,
40.00% Al.

Annealed at 135°C for three weeks.
Consists nearly completely of eutectic
of the lamellar type. Magnification
approx. 80X.

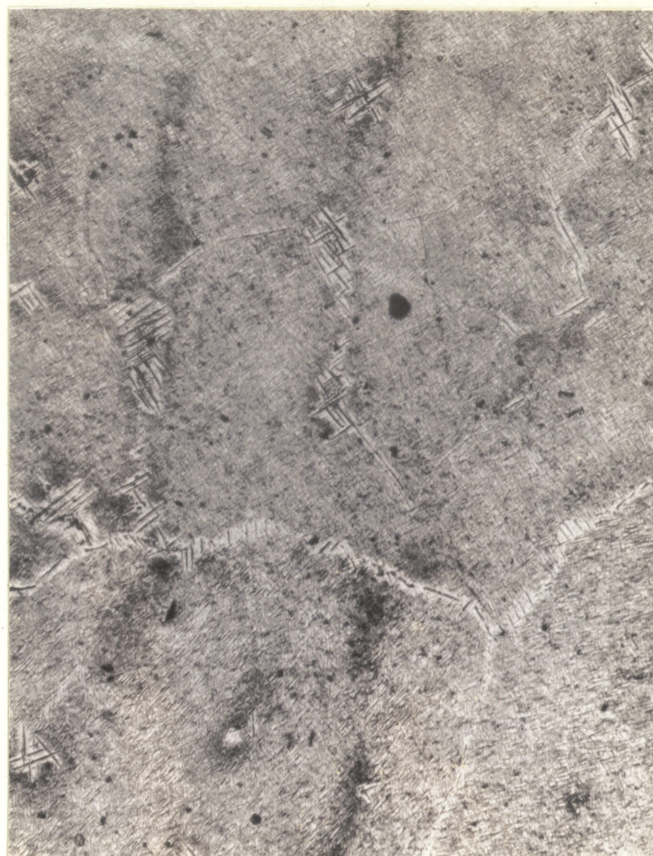


PLATE 22

ALLOY NO. 2 , COMPOSITION 20.00% Ag,
80.00% Al

Annealed at 135°C for three weeks.
Needle-like ζ -phase precipitate at the
grain boundaries can be seen. Magnifi-
cation approx. 80X.



PLATE 23

ALLOY NO. 15, COMPOSITION 60.00% Ag,
30.00% Al,
10.00% In

Annealed at 135°C for three weeks. Evidently a two-phase alloy. Darker σ -phase grains separated by γ -phase (lighter areas) Magnification approx. 80X.



PLATE 24

ALLOY NO. 26 COMPOSITION 59.98% Ag,
20.00% Al,
20.00% In

Annealed for three weeks at 135°C
Careful Scrutiny shows that three
phases are present, σ , ϵ and γ .
Magnification approx. 80X.

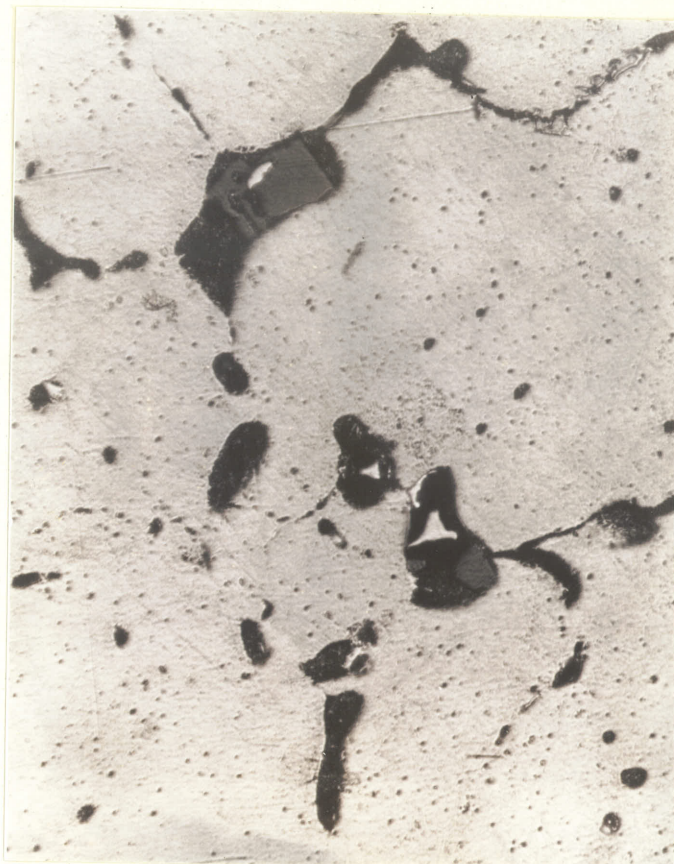


PLATE 25

ALLOY NO. 10, COMPOSITION 10.02% Ag.
80.00% Al,
10.02% In.

Annealed at 135°C for three weeks. The major phase is σ -phase. A small amount of ϕ -phase is present (grey) and a very small amount of ϵ -phase (light) is also present. Magnification approx. 80X.

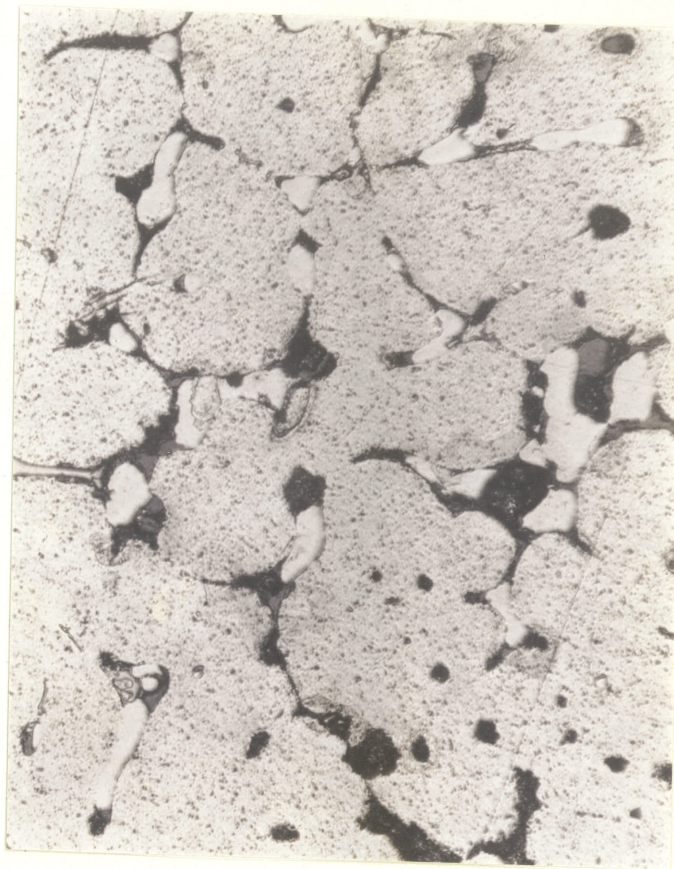


PLATE 26

ALLOY NO. 22, COMPOSITION 20.00% Ag,
60.00% Al,
20.00% In.

Annealed at 135°C for three weeks. It is a three-phase alloy with σ (major), ϵ (small light areas) and some δ -phase (smooth grey) present. Some metastable In-phase is also present. Magnification approx. 80X.

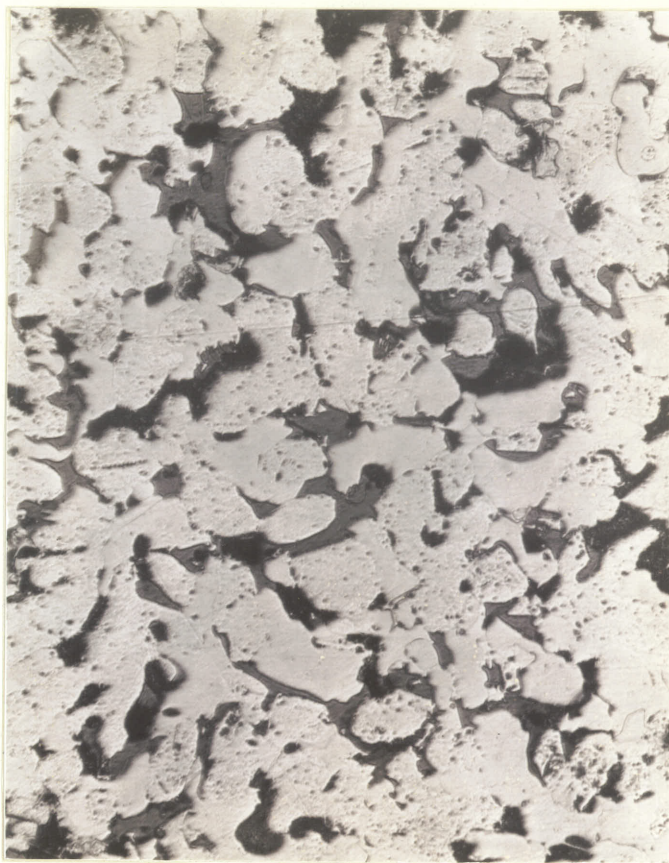


PLATE 27

ALLOY NO. 34, COMPOSITION 50.00% Ag,
19.99% Al,
30.00% In,

Annealed at 135°C for three weeks. Three phases are present: σ (light "spongy"), ϵ (light smooth) and δ (smooth grey). Magnification approx. 80X.

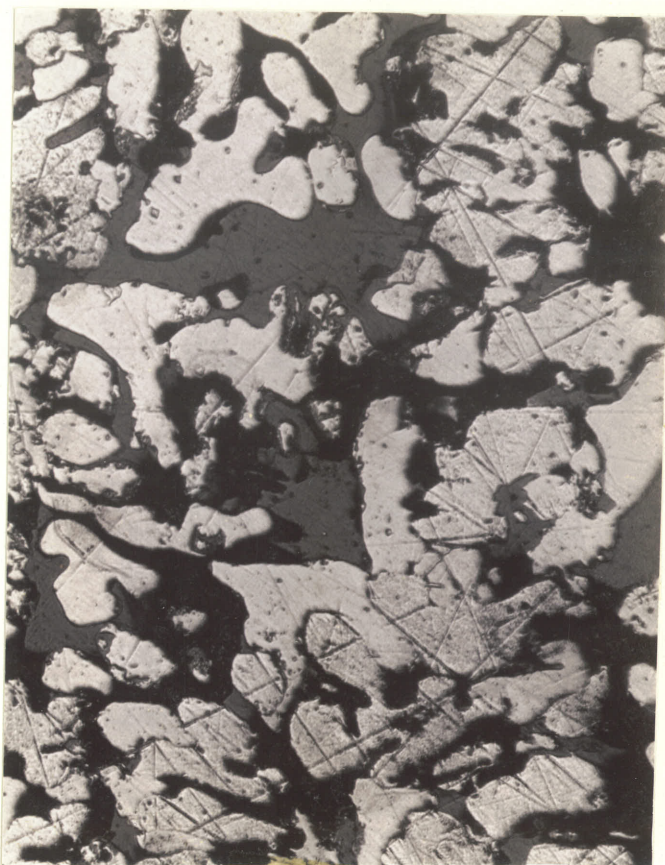


PLATE 28

ALLOY NO. 41, COMPOSITION 40.00% Ag,
20.00% Al,
39.99% In,

Annealed at 135°C for three weeks. Three
phases are present: σ (light scratched), ϵ
(light smooth), and δ (dark grey smooth).
Magnification approx. 80X.

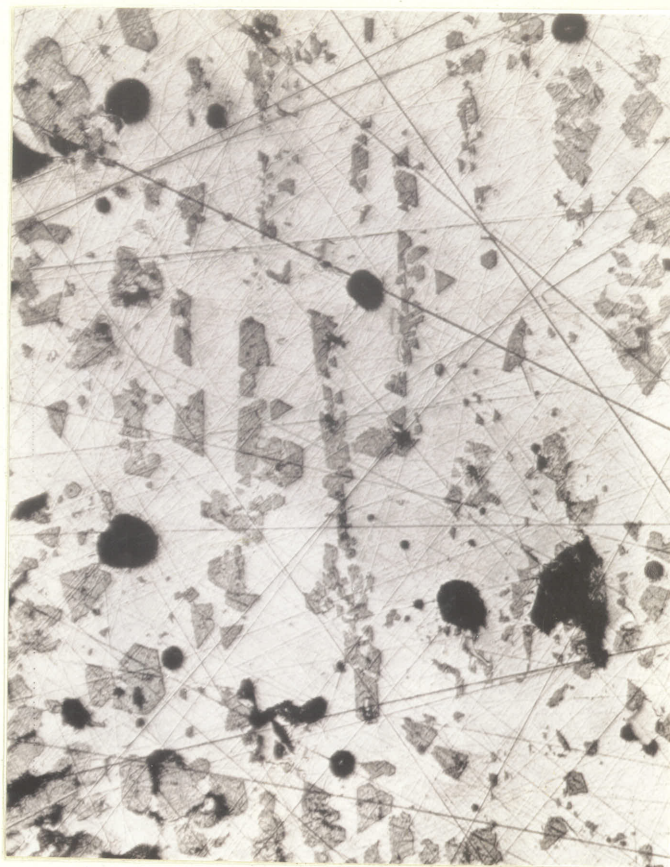


PLATE 29

ALLOY NO. 48, COMPOSITION 40.00% Ag,
10.00% Al,
49.99% In

Annealed at 135°C for three weeks. This alloy consists of ϵ -phase, ϕ -phase (brown) and a very small amount of σ -phase. The black areas are holes. Magnification approx. 80X.

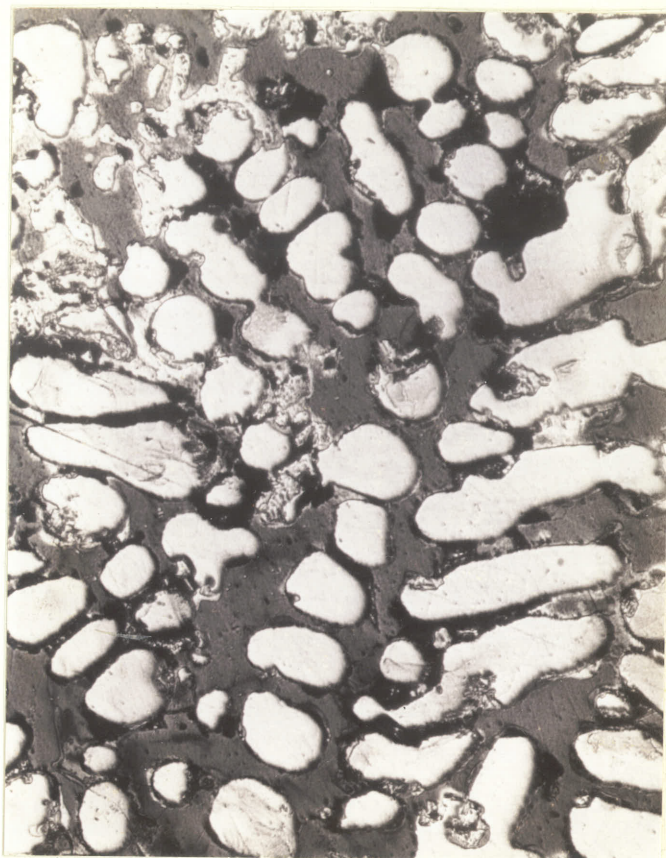


PLATE 30

ALLOY NO. 42, COMPOSITION 49.99% Ag,
10.00% Al,
40.00% In,

Annealed at 135°C for three weeks. This alloy consists of ε-phase (light areas) within the σ-phase (grey) and a small amount of σ-phase. Magnification approx. 80X.

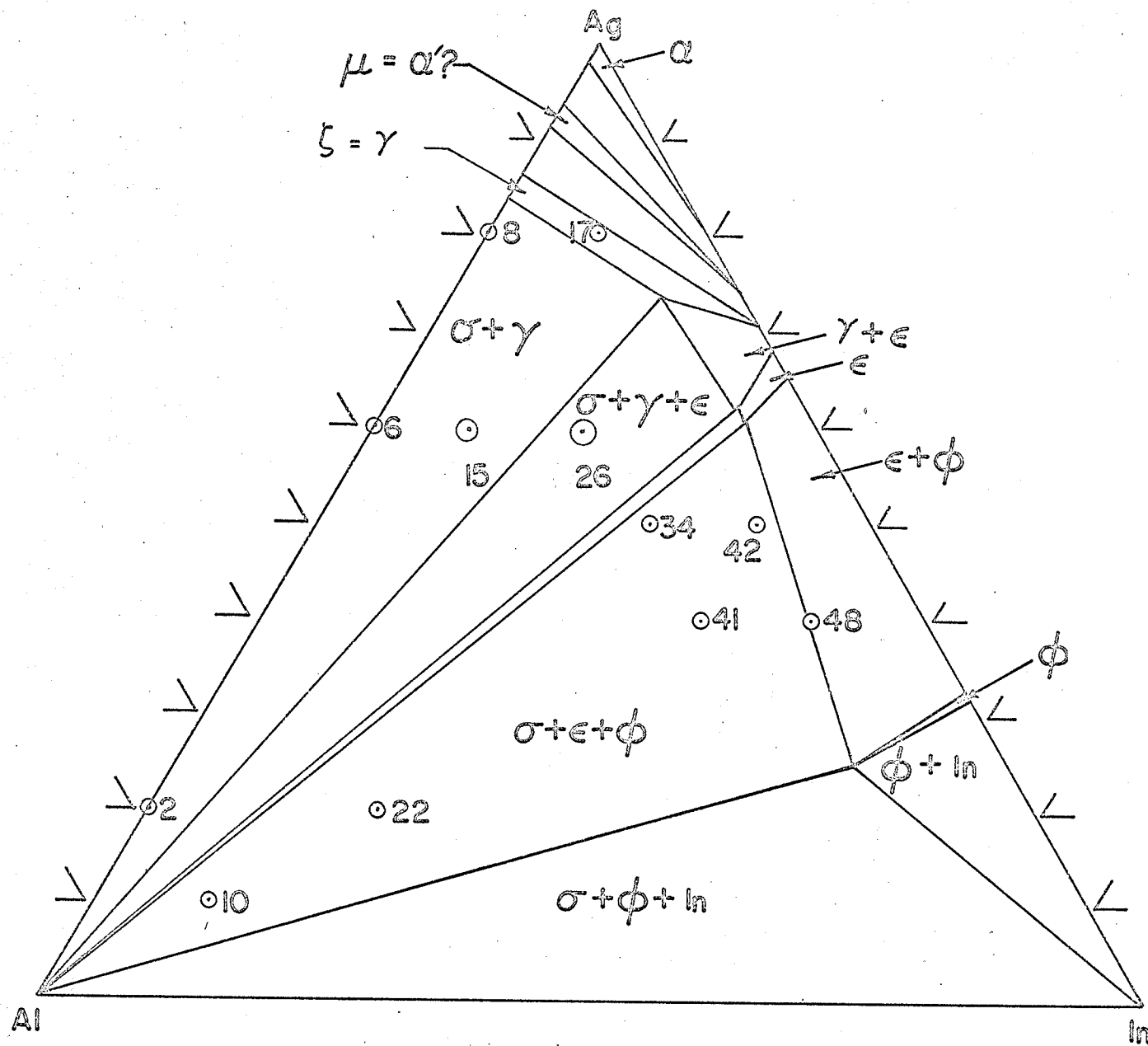


Fig. 21. Room Temperature Isothermal Section

The Room Temperature Isothermal Section

At room temperature, all phases are solid (Fig. 21). Three three-phase areas exist, viz. $(\sigma + \delta + \epsilon)$, $(\sigma + \gamma + \epsilon)$ and $(\sigma + \delta + \text{In})$. No two-phase area $(\delta + \sigma)$ is shown. These phase boundaries have been drawn in accordance with the microstructure of annealed alloys observed under the microscope and shown in the photomicrographs of Plates 20 to 30. In addition to the ternary alloys, three binary alloys in the system, Ag-Al, were examined, mainly to see how the microstructure of these alloys changes after indium is added. Alloys #8, #6 and #2 are the binary alloys shown in Plates 20, 21, and 22 respectively. The first shows large grains of ζ -phase and some eutectic. The second alloy Plate 21 is very nearly of the eutectic composition, and the lamellar type of eutectic is seen. Alloy #2, Plate 22 shows the needle-like ζ -phase precipitate at the grain boundaries within the σ -phase (or Al-phase). The "spongy" appearance of the σ -phase is a characteristic of this phase in the ternary system also.

Alloy # 15, Plate 23, is basically the same type of alloy as #8, except that no eutectic is present. It is a binary alloy consisting of $(\sigma + \gamma)$ phases.

Alloy #26, Plate 24, looks very much like #15, but a third phase can be discerned. The poor quality of this photograph makes it difficult to identify the phases. Under the microscope the third phase was seen much better. This alloy consists of three phases, $(\sigma + \gamma + \epsilon)$ and a small amount of metastable indium phase.

Alloys #10, 22, 34, and 41, have the same kind and number of phases;

only the relative amounts of phases vary. These are shown in Plates 25, 26, 27 and 28 respectively. They are all three-phase alloys ($\sigma + \epsilon + \phi$). The "spongy" looking, easily scratchable σ -phase, is present in all four alloys. The characteristic colour of the ϕ -phase (dark grey and brown under the microscope) was also easily identified in all three alloys. The ϵ -phase (bright) is present in Alloy #10, Plate 25 in only very small quantity. A small amount of metastable indium phase seems to be present as well.

Alloy #42, Plate 30, consists of ϵ -phase embedded in ϕ -phase and a very small amount of σ -phase is still present. This alloy is still within the three-phase region ($\sigma + \epsilon + \phi$).

Alloy #48, Plate 29 consists of only two phases, " ϕ " and " ϵ ", with a minute amount of σ -phase discernible. This alloy is considered to lie on the boundary, as shown in the "Room Temperature Section" of Fig. 21.

Alloy #17, of composition 80.00% Ag, 10.00% Al, 10.00% In, was also annealed for three weeks at 135°C and examined under the microscope, and found to be homogeneous (γ).

The γ -phase of the binary system, Ag-In, and the ζ -phase of the, Ag-Al system, are both close-packed hexagonal with similar cell edges:

$$\gamma(\text{at r.t.}): a = 2.961 \text{ \AA}; c = 4.778 \text{ \AA}$$

$$\zeta : a = 2.865 \text{ \AA}; c = 4.653 \text{ \AA} \quad (66)$$

In view of this, these two fields of homogeneity in the respective binary systems have been joined in the ternary system. Alloy #17 falls within this homogeneous field in the ternary system.

The nomenclature of the ternary phases is the same as that of the binary system, Ag-In, with one symbol added, viz, " σ ", which is used for the aluminium α -solid-solution in the ternary system. It was used by most workers for the same phase in the , Ag-Al, system.

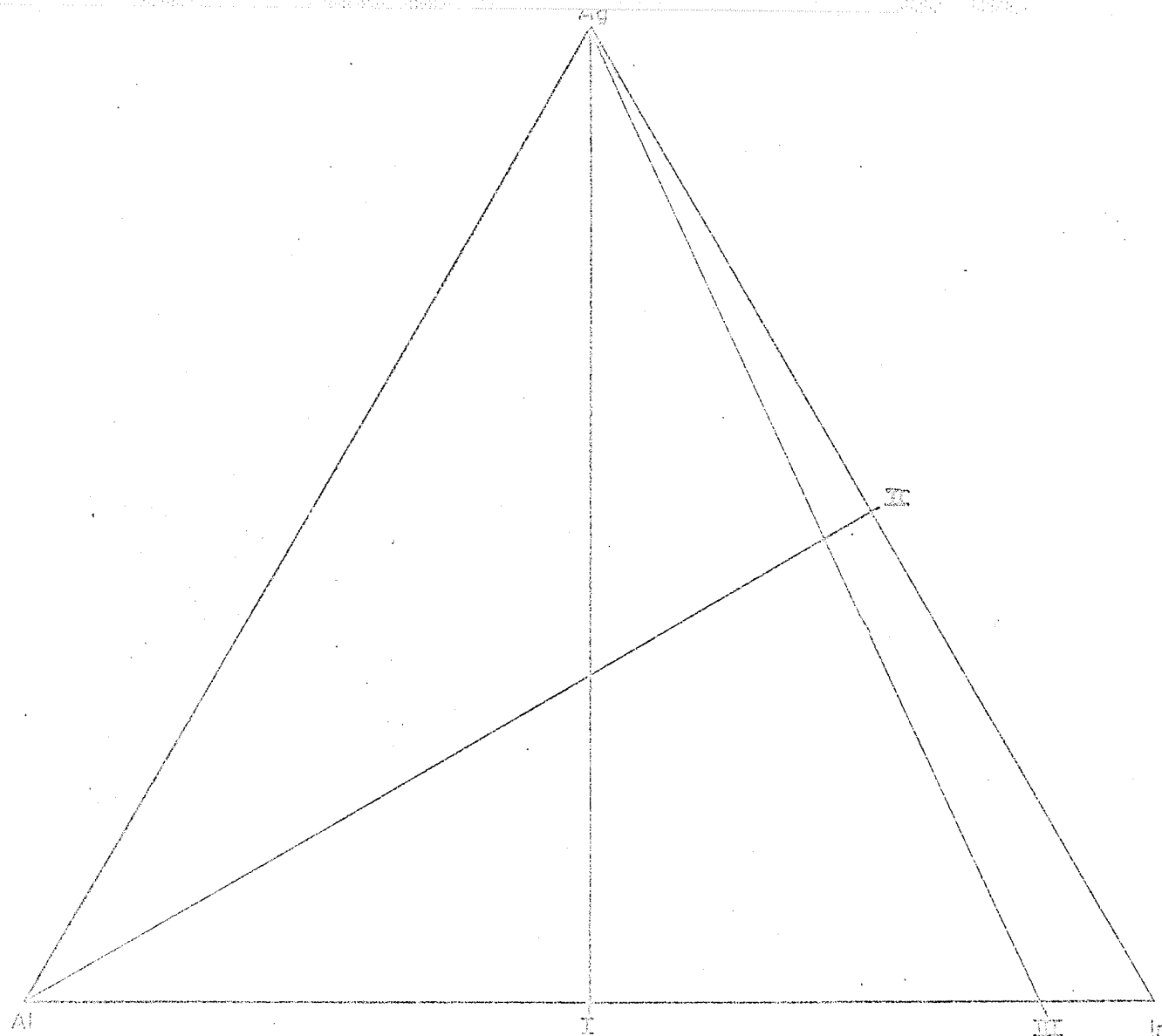


Fig. 16. Plan of "Vertical Sections".

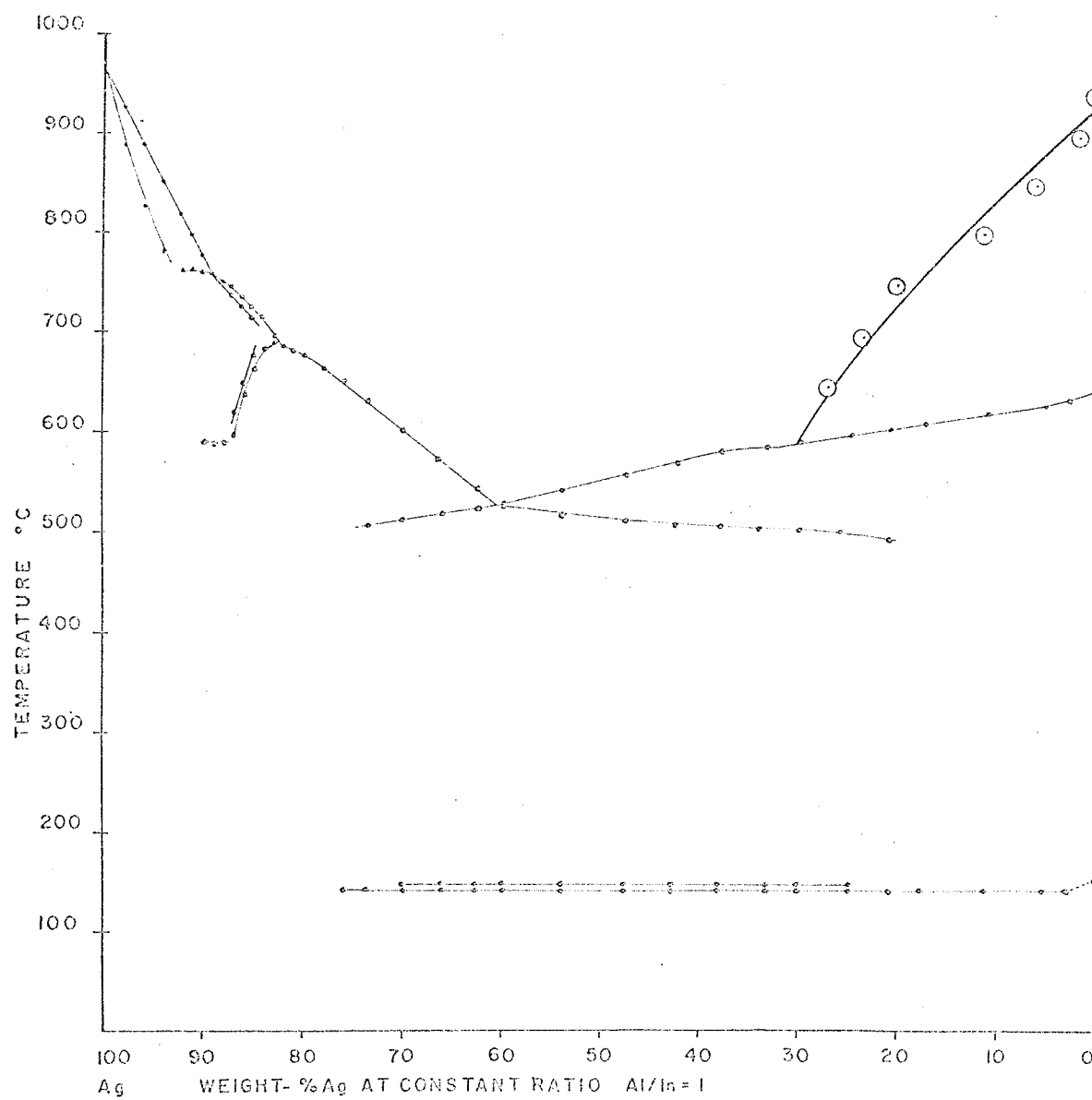


Fig. 17. Vertical Section I

TABLE 12

THERMAL ANALYSIS DATA, VERTICAL SECTION I

	Composition in Weight - %			Temp. °C Liquidus	Temp. °C Inflections	Temp. °C Halts
	In	Ag	Al			
1	1.00	98.00	1.00	921	884	
2	1.96	96.08	1.97	887	822	
3	3.00	94.00	3.00	849	779	
4	4.00	92.00	4.00	814	760	
5	4.50	91.00	4.50	796	762	
6	5.00	90.00	5.00	774	761	590
7	5.50	89.00	5.50	757		588
8	7.00	88.00	6.00	748		588
9	6.50	87.00	6.50	742	737	
					613	
					597	
10	7.00	86.00	7.00	732	722	
					699	
					635	
11	7.50	85.00	7.50	724	713	
					678	
					663	
12	8.00	84.00	8.00	712	682	
13	8.50	83.00	8.50	697	690	
					375	
14	9.00	82.00	9.00	688		
15	9.50	81.00	9.50	683		
16	10.00	80.00	10.00	678		
17	11.01	77.99	11.00	663		
18	12.00	76.00	12.00	652		143
19	13.27	73.46	13.27	631	507	144
20	15.01	69.99	15.00	601	512	143
						148
21	16.91	66.19	16.90	573	518	143
						148
22	18.76	62.49	18.75	546	522	143
					483	147
					459	
23	20.01	59.99	20.00	528	524	143
						148
24	23.00	54.02	22.98	542	518	143
						148
25	26.26	47.50	26.25	559	512	143
						147
26	28.64	42.72	28.64	570	510	143
					163	147

Table 12 (Continued)

	<u>Composition in Weight - %</u>			Temp. °C Liquidus	Temp. °C Inflections	Temp. °C Halts
	In	Ag	Al			
27	31.03	37.94	31.03	581	506 188 165	143 148
28	33.27	33.37	33.36	588	507	143 148
29	35.01	29.99	35.00		591 506	144 149
30	37.51	24.99	37.50		600 503	141 148
31	39.52	20.97	39.51		606 494	143
32	41.11	17.79	41.10		611	143
33	44.41	11.20	44.40		621	143
34	47.31	5.40	47.30		629	143
35	48.51	3.00	48.50		635	143
36	50.01	49.99			644	154

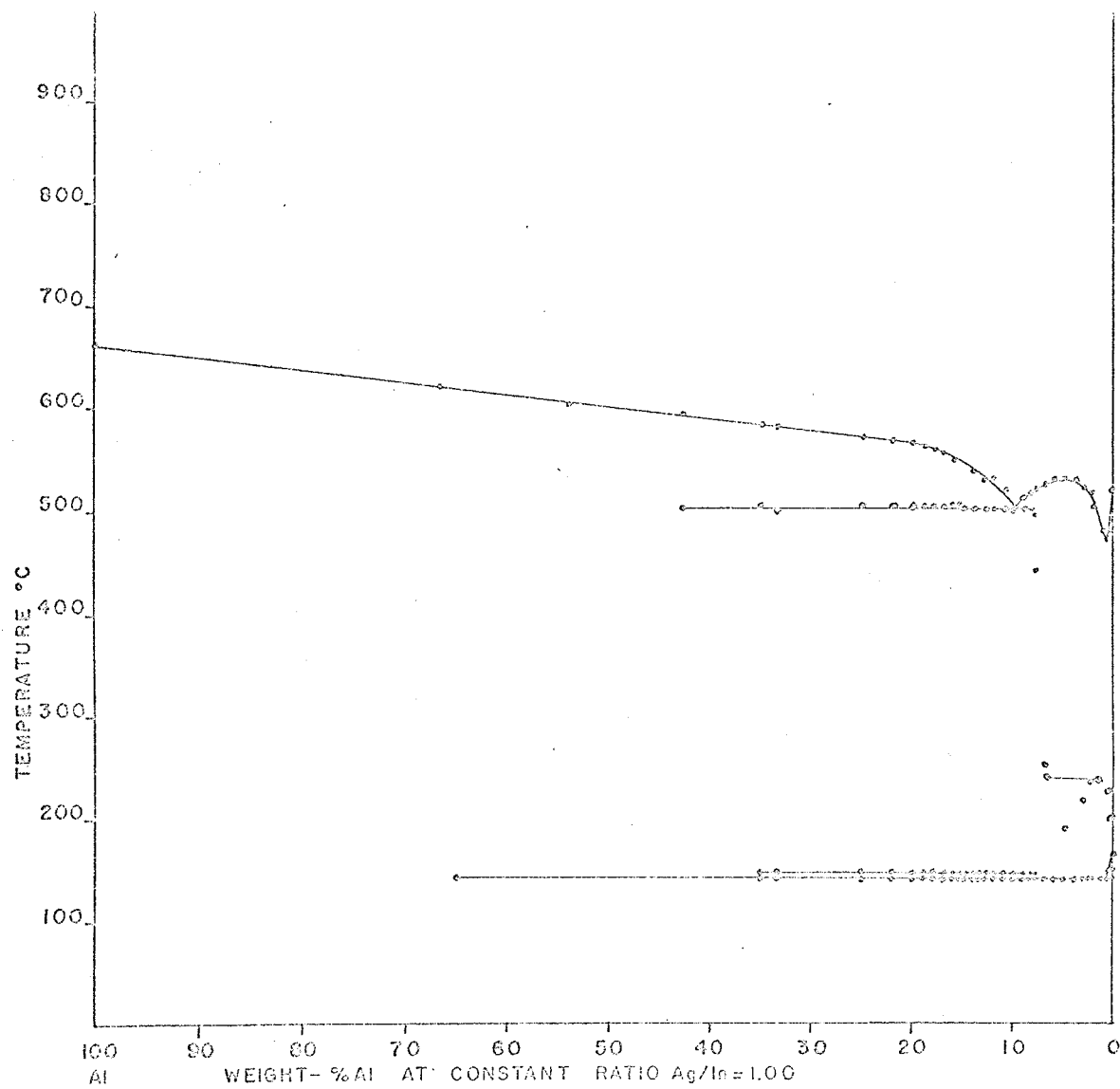


Fig. 18. Vertical Section II

TABLE 13

THERMAL ANALYSIS DATA, VERTICAL SECTION II

	<u>Composition in Weight %</u>			Temp. °C Liquidus	Temp. °C Inflections	Temp. °C Halts
	In	Ag	Al			
37	50.00	50.00		525		207 166 143
38	49.75	49.75	.50	482	232 152 164	143
39	49.49	49.49	1.01	483	178 159	143
40	49.00	49.00	2.00	509	403 398 330 323	239 147 143
41	48.75	48.75	2.50	521		239 147 144
42	48.50	48.50	3.00	528		241 ----- 143 ----- ----- 141
43	48.01	48.01	3.98	173		
44	47.50	47.50	5.00	537	482 192 150	241 143 143
45	47.00	47.00	6.00	533		
46	46.50	46.50	7.00	528	154 192	243 141
47	46.00	46.00	8.00	524	500 447	148 143
48	45.81	45.81	8.38	520	503 447	147 143
49	45.46	45.46	9.09	516		505 148 143
50	45.00	45.00	10.00	510	442	506 148 143
51	44.50	44.50	11.00	524	334	506 149 143
52	44.00	44.00	12.00	536	273	506 148 143

Table 13 Continued

	<u>Composition in Weight %</u>			Temp. °C Liquidus	Temp. °C Inflections	Temp. °C Halts
	In	Ag	Al			
53	43.50	43.50	13.00	532	199	506 148 143
54	43.25	43.25	13.50	532	179	507 148 143
55	43.00	43.00	14.00	541	172	507 148 143
56	42.50	42.50	15.00	546	348 177	506 148 143
57	42.25	42.25	15.50	547	435	510 148 143
58	41.98	41.98	16.04	554		510 148 143
59	41.50	41.50	17.00	561		508 148 143
60	41.00	41.00	18.00	563		508 148 143
61	40.50	40.50	19.00	567		508 148 143
62	40.00	40.00	20.00	569		507 148 143
63	39.00	39.00	22.00	571		587 148 143
64	37.50	37.50	25.00	576		506 149 143
65	33.27	33.37	33.36	587		506 149 144
66	32.50	32.50	35.00	588		507 148 143
67	28.60	28.60	42.80	599		505

Table 13 Continued

	<u>Composition in Weight %</u>			Temp. °C Liquidus	Temp. °C Inflections	Temp. °C Halts
	In	Ag	Al			
68	23.00	23.00	54.00	609	457	
69	16.80	16.80	66.40	623		
			100.00	659		143

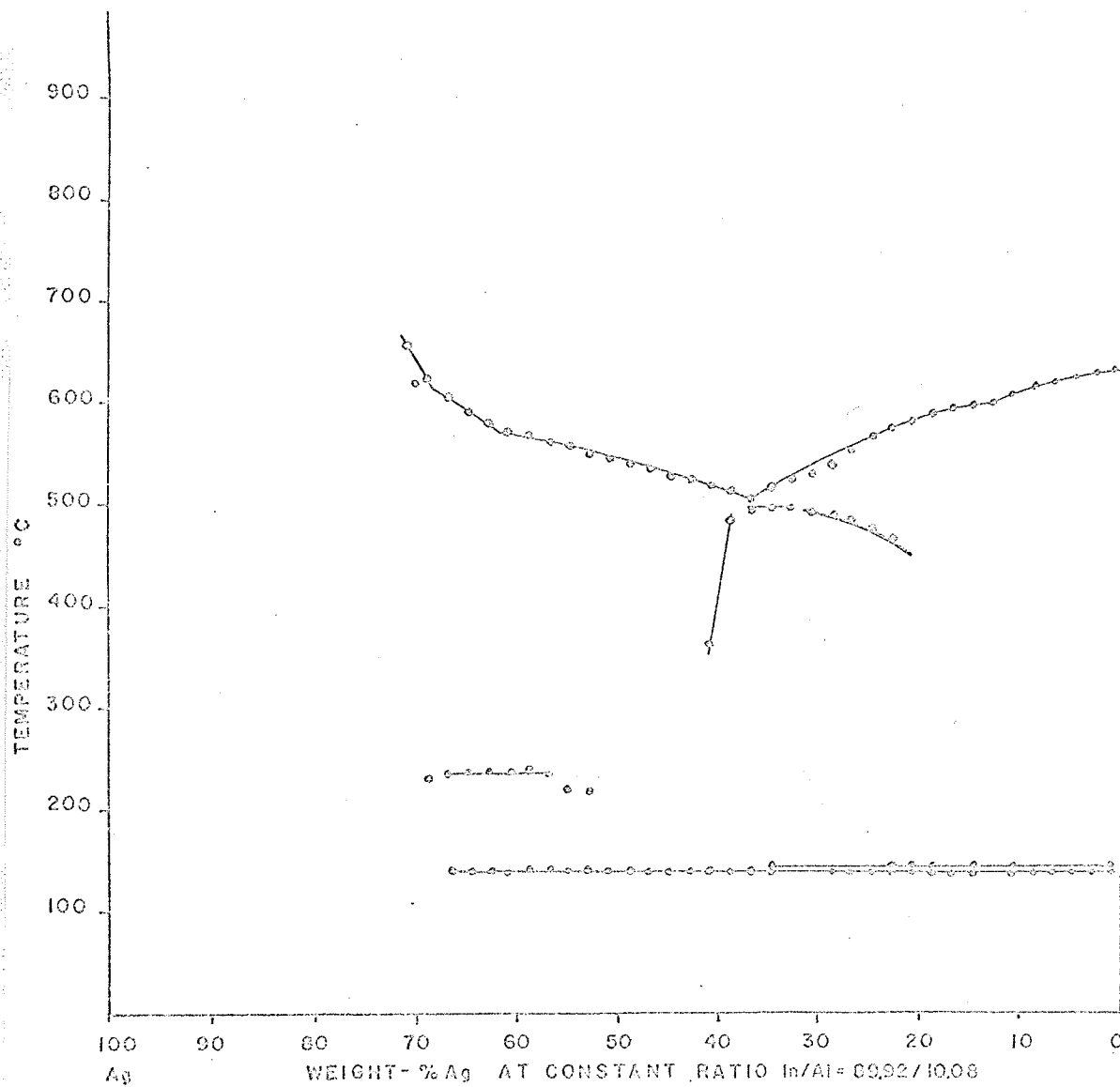


Fig. 19. Vertical Section III

TABLE 14

THERMAL ANALYSIS DATA, VERTICAL SECTION III

	<u>Composition in Weight %</u>			Temp. °C Liquidus	Temp. °C Inflections	Temp. °C Halts
	In	Ag	Al			
70	89.11	.90	9.99	639		148
71	87.22	3.00	9.78	634		143
72	85.43	5.00	9.57	631		143
73	83.63	7.00	9.37	628		143
74	81.83	9.00	9.17	622		143
75	80.03	11.00	8.97	614		148
76	78.23	13.00	8.77	609		143
77	76.43	15.00	8.57	605		148
78	74.63	17.00	8.37	601		143
79	72.84	19.00	8.16	595		148
80	71.04	21.00	7.96	589	458	150
81	69.24	23.00	7.76	581	473	143
82	67.44	25.00	7.56	572	483	149
83	65.64	27.00	7.36	560	490	143
84	63.84	29.00	7.16	549	495	143
85	62.05	31.00	6.95	539	499	143
86	60.25	33.00	6.75	531	504	143
87	58.45	35.00	6.55	524	502	148
88	56.62	37.04	6.35	512	501	143
89	54.85	39.00	6.15	520	490	143
90	53.05	41.00	5.95	527	368	143
91	51.25	43.00	5.74	531		143
92	49.46	45.00	5.54	533		143

Table 14 Continued

	<u>Composition in Weight %</u>			Temp. °C Liquidus	Temp. °C Inflections	Temp. °C Halts
	In	Ag	Al			
93	47.66	47.00	5.34	541		143
94	45.86	49.00	5.14	548		143
95	44.06	51.00	4.94	552		143
96	42.26	53.00	4.74	556	222	143
97	40.46	55.01	4.53	562	227	144
98	38.67	57.00	4.33	568		240
						145?
						143
99	36.87	59.00	4.13	573		242
						145
100	35.07	61.00	3.93	576		241
						143
101	33.27	63.00	3.73	584		241
						143
102	31.47	65.01	3.53	597		240
						143
103	29.67	67.00	3.33	611		240
						143
104	27.87	69.00	3.12	630	235	
105	26.08	71.00	2.92	662	625	

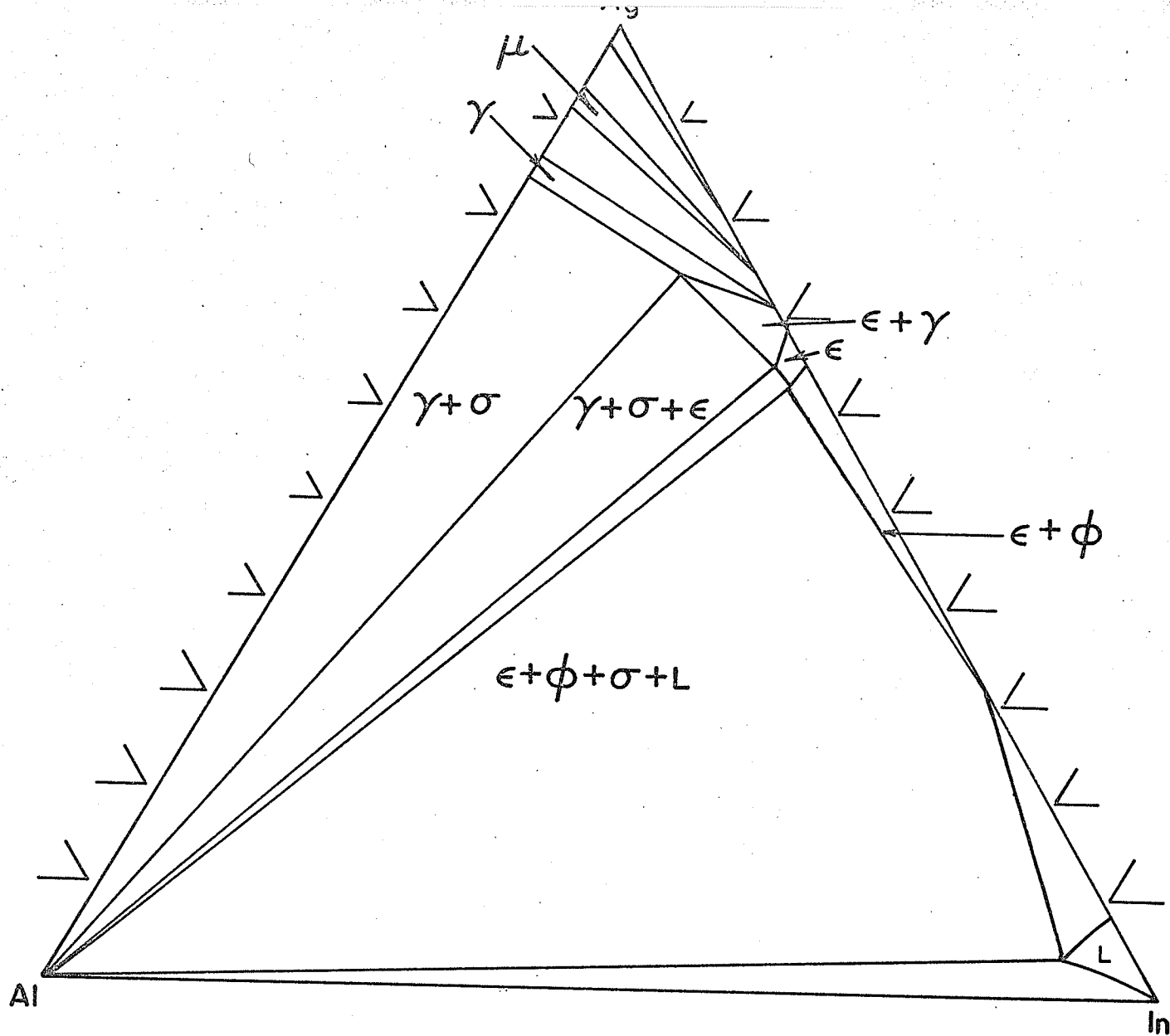


Fig. 22. 148°C Isothermal Section

The 148°C Isothermal Section

The section shown in Fig. 22 was constructed from experimental data of the "Vertical Sections" in Figs. 17, 18, and 19, a knowledge of the contiguous binary systems, some information obtained in previous work (71), and application of the phase rule.

The "Vertical Sections" show that the binary peritectic isotherm of 166°C of the system, Ag-In, terminates on the invariant plane at 148°C (Tables 12, 13, 14). The horizontal lines or isotherms of the "Vertical Sections I, II, III" Figs. 17, 18, and 19, represent cuts through the invariant plane in the three dimensional system. The invariant plane must be bounded by straight lines, since in three dimensions it is bounded by ruled surfaces.

It is known from the location and direction of the ternary troughs (71) that a peritectic type of equilibrium is involved at the 148°C invariant plane. The composition of the four phases at 148°C will determine the four apices of the invariant plane. Which four phases are involved in the equilibrium and their approximate composition, were deduced as follows: In the binary system, Ag-In, Fig. 2, the equilibrium phases of the peritectic reaction at 166°C are the two solid phases ϵ and ϕ and the liquid of 95.5 per cent indium. The same three phases must be involved in the four-phase equilibrium at 148°C (the invariant plane) in the ternary system, since this binary peritectic terminates on the invariant plane. It will be noted that in the binary system (Al-In) Fig. 4 nearly pure aluminium (σ phase as it is called in the ternary) is in equilibrium with nearly pure liquid indium

(less than 1% Al) at 166°C. The composition of the liquid at 148°C in the ternary system (equilibrium phase at the invariant plane) was found by chemical analysis of five different alloys with an overall composition within the area of the invariant plane

OVERALL COMP.

% Ag	% Al	In
40.00	20.00	39.99
49.99	10.00	40.00
30.00	20.00	50.00
29.99	10.00	60.00
20.00	60.00	20.00

The average composition of the liquid present in these alloys at 150°C was 89% In, 5% Ag, 6% Al. The error is probably $\pm 2\%$ in indium and the same in aluminium (obtained by subtraction), and negligible in silver. The alloys were first annealed at 135°C for three weeks and then heated to 150°C and kept at this temperature for approximately an hour; little droplets of liquid alloy were seen to ooze out of the alloy after it was heated to this temperature. The droplets of liquid solidified to globules of alloy high in indium after the alloy was cooled to room temperature. These globules of each alloy were collected and analyzed by titration and polarography as described under "Experimental Techniques". Assuming that the difference in composition of the liquid at 150°C and 148°C is not great, the analysis gave the composition of the liquid in equilibrium with the three solid phases σ , ϵ , and ϕ at the invariant plane in Fig. 22. It is known from the binary phase diagram, In-Al, (Fig. 4,) that the σ phase (or nearly pure aluminium) can be in equilibrium with a liquid of high indium concentration

and that no intermediate phases exist at 148°C . It follows that in the ternary system at this temperature the liquid high in indium (89% In) is also in equilibrium with the σ phase. The four equilibrium phases at 148°C are ϵ , ϕ , σ and liquid of the given composition. Neither silver nor indium dissolve in solid aluminium at 148°C to an appreciable extent, (less than one percent) as can be seen from the appropriate binary systems Figs. 6 and 4. Therefore, in the ternary system the σ phase will also be nearly pure aluminium and two corners of the invariant plane are fixed. The ϵ -phase has a composition range of two percent in the binary system Ag-In. This field of homogeneity in the binary system would be expected to extend somewhat into the ternary system. In this connection two conditions must be imposed. Firstly, the 148°C isotherms of the "Vertical Sections II and III" (Figs. 18, and 19), when transferred to the isothermal section should fall within the area of the invariant plane. Secondly, to be thermodynamically sound, the boundaries of the single-phase region (where they meet the invariant plane) when extended, must both lie within or outside the invariant area but one cannot extend into the invariant area and the other be outside of it (4,5). For the sake of brevity, this will be called the "principle of extension". Bearing these points in mind, I have drawn the isothermal plane as shown in Fig. 22.

The composition of the ϕ -phase in the ternary system was not established. Since the ϕ -phase has a composition range of less than two per cent in the binary system, it is reasonable to assume that the ϕ -phase field would extend very little into the ternary system. In support of this assumption, two points can be made: Both the ϕ -phase and indium have tetra-

gonal structures, solid indium does not dissolve aluminium at 148°C , and the isothermal plane at 143°C (eutectic) abutts the binary Ag-In. The indications are that the ternary composition of the ϕ -phase (at 148°C) lies very near the edge of the invariant plane.

The equilibrium of the invariant plane is as follows

$L + \epsilon \rightleftharpoons \sigma + \phi$. This is the type of reaction called by Zernike (70) "the peritectic of the second kind". Slightly above 148°C , an isothermal section would show two triangular regions with phases $L + \epsilon + \phi$ and $L + \epsilon + \sigma$. Slightly below the temperature of the invariant plane an isothermal section would show two triangular regions with the phases $\epsilon + \phi + \sigma$ and $L + \phi + \sigma$, respectively, depending on the overall composition of the alloy.

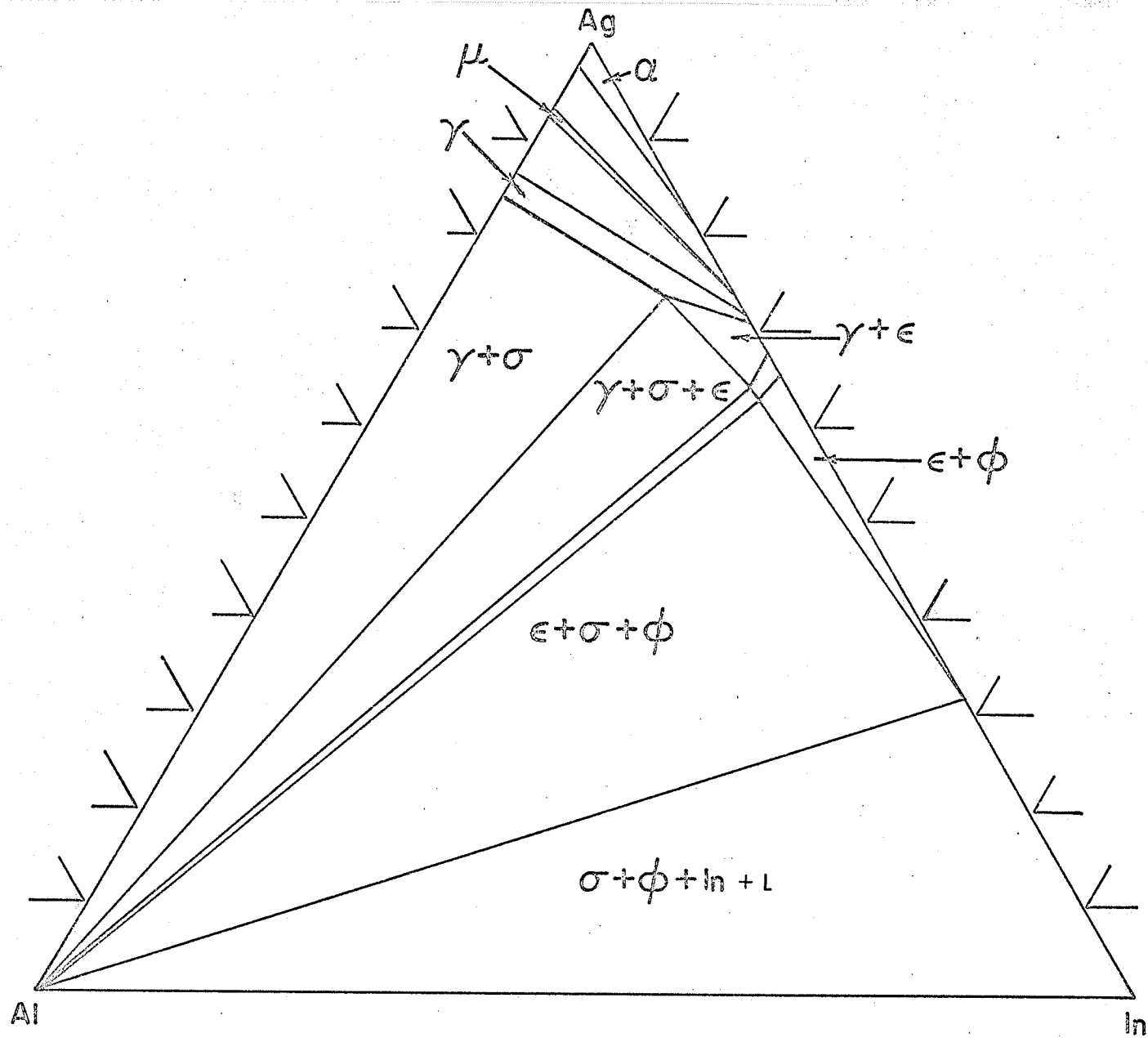


Fig. 23. 143°C Isothermal Section

The 143°C Isothermal Section

This section is shown in Fig. 23. The invariant plane has its apices at the three solid phases σ , ϕ and In. The transformation at this temperature is of the ternary eutectic type: $L \rightleftharpoons \phi + \sigma + \text{In}$. The composition of the liquid in equilibrium with the three solids was estimated (from the intersection of the ternary troughs (71)) to be 95% In, 4% Ag, 1% Al. Due to the very narrow range of homogeneity of the phase " ϕ " the two phase field ($\phi + \sigma$) is not shown in this section. The three-phase field ($\epsilon + \sigma + \phi$) adjoining the invariant plane represents a limiting case.

Since the location of the phase boundaries is not expected to change noticeably in the temperature interval of 5°C this isothermal section is the same in other respects as the 148°C isothermal section.

TABLE 15

X-RAY DIFFRACTION DATA OF OBINATA AND HAGIYA (45)

I	h^2	$\sin^2 \theta$	$\frac{\sin^2 \theta}{h^2}$	FOR Ag_3Al (μ)			hkl cubic	hk.l phase	d*** (Hexa.) ($\text{\AA}$) phase
				d^* ($\text{\AA}$)	a ($\text{\AA}$) cal.	d^{**} ($\text{\AA}$) cubic			
V. Str.	9	0.112	0.01244	2.30	3.990	2.34	1 1 1		
V. Str.	10	0.125	0.01250	2.18				10.1	2.19
Str.	11	0.137	0.01245	2.08	4.165	2.03	2 0 0		
m	14	0.175	0.01250	1.84	4.121	1.81	2 1 0		
w	17	0.210	0.01235	1.682				10.2	1.697
Str.	18	0.225	0.01250	1.625	3.981	1.654	2 1 1		
Str.	20	0.250	0.01250	1.542				00.3	1.551
V. Str.	26	0.326	0.01254	1.350	4.050	1.350	3 0 0		
V. Str.	29	0.364	0.01255	1.278	4.041	1.281	3 1 0		
Str.	30	0.375	0.01250	1.259				20.0	1.241
m	35	0.436	0.01246	1.167	4.044	1.169	2 2 2		
m	36	0.450	0.01250	1.149				00.4	1.163
w	37	0.462	0.01249	1.134					
m	38	0.472	0.01253	1.122	4.046	1.124	3 2 0		
w	41	0.507	0.01237	1.083	4.051	1.083	3 2 1		
w	43	0.535	0.01244	1.054				11.3	1.052
w	45	0.561	0.01247	1.029	4.117	1.014	4 0 0		
m	49	0.607	0.01239	0.990	4.080	0.983	4 1 0		
m	50	0.620	0.01240	0.979				20.3	0.969
m	53	0.656	0.01238	0.952	4.038	0.955	4 1 1		
m	54	0.667	0.01235	0.944				21.0	0.938
m	56	0.694	0.01239	0.925	4.034	0.929	3 3 1		
m	57	0.704	0.01236	0.919				21.1	0.919
Str.	59	0.730	0.01237	0.902	4.035	0.906	4 2 0		
V. Str.	61	0.754	0.01236	0.888				11.4	0.903
Str.	62	0.765	0.01234	0.881	4.039	0.884	4 2 1		

Table 15 Continued

I	h^2	$\sin^2 \theta$	$\frac{\sin^2 \theta}{h^2}$	d^* (Å)	a (Å) cal.	d^{**} (Å) cubic	hkl cubic	hk.l phase	d^{***} (Hexa) (Å) phase
Str.	64	0.789	0.01233	0.868				21.2	0.870
w	65	0.805	0.01239	0.859	4.030	0.864	3 3 2		
Str.	66	0.820	0.01242	0.851				20.4	0.849
w	68	0.842	0.01238	0.840					
w	69	0.857	0.01242	0.833	4.080	0.827	4 2 2		
Str.	70	0.869	0.01241	0.827				30.0	0.827
w	72	0.891	0.01238	0.817				30.1	0.814
Str.	74	0.915	0.01236	0.806	4.030	0.810	5 0 0	21.3	0.803
			0.01243		4.051				
			$a = 6.91 \text{ Å}$		± 0.026				

* Calculated using $\sin^2 \theta$

** Calculated using $a = 4.051$

*** Calculated using $a = 2.865 \text{ Å}$

$c = 4.653$ (66).

The μ -Phase and the α' -Phase in the Ternary System

The crystal structure of the phase " μ " in the binary system, Ag-Al, at the composition Ag_3Al was investigated by Westgren and Bradley (63) and by others (36,45,65); it was found to be cubic of the β -manganese type, with a cell edge of $6.916 \text{ \AA}$ (65). On the left-hand side of Table 15 the x-ray diffraction data of Obinata and Hagiya (45) are reproduced for the alloy Ag_3Al , (μ). On the right hand side two sets of d-values are calculated and compared with those of Obinata and Hagiya (45). One set of d-values and the corresponding (hkl) indices are for the cubic primitive with cell edge $a = 4.051 \text{ \AA}$ and the other set of d-values and their corresponding (hk.l) indices are for the hexagonal ζ -phase of the system Ag-Al, with cell edges $a = 2.865 \text{ \AA}$, $c = 4.653 \text{ \AA}$ (66). It should be noted that the above cell edges apply to 200°C and the agreement between the calculated d-values for the hexagonal phase and the observed d-values of Obinata and Hagiya is therefore not as good as it could be if the cell edges that fit best the experimental data had been used to calculate the d-values. Under "a Calc." in Table 15, a cubic cell edge has been calculated for all lines indexed as cubic, in order to show that a reasonably constant cubic cell edge value is indeed obtained from such lines.

It is well known that solid state transformations are slow and usually incomplete. The phase in question (μ) is formed by a peritectoid solid state reaction at 448°C (33). It is in such cases possible to have two phases present where one phase should be present at equilibrium. In this case, the diffraction data of Table 15 are for the composition Ag_3Al

(7.98% Al), and since the field of the μ -phase is much narrower near the transformation temperature than at lower temperatures, this alloy consists of ζ , a little above the transformation temperature, but at room temperature this alloy should be μ -phase, as can be seen from the binary phase diagram of Fig. 6. If the transformation to the equilibrium phase " μ " at room temperature is not complete, then the alloy remains heterogeneous, consisting of ($\mu + \zeta$) phases. (The β -phase is not retained at room temperature.) Based on this reasoning the diffraction data of Obinata and Hagiya (45) were indexed as if the alloy Ag_3Al was heterogeneous. When this is done the lines of the cubic μ -phase can be indexed on a smaller cell edge than previously viz. $4.051 \text{ \AA}$. This cell edge is very near that for the silver α -solid solution at the phase boundary viz. 4.0587 (at 200°C) as given by Ageew and Shoyket (43). Using this cell edge and those for the hexagonal phase, d-values are calculated and are given in columns d^{**} and d^{***} respectively. A comparison with the d-values in column d^* which are the values of Obinata and Hagiya (45) (they were calculated from $\sin^2\theta$) shows that the observed d-values can all be reproduced (except for two weak lines) reasonably well by assuming that the alloy consists of the hexagonal phase ζ and a cubic primitive phase having a cell edge of $4.051 \text{ \AA}$. It is not merely coincidence, I think, that the agreement is so good. The suggestion presents itself that a situation exists in the system Ag-Al similar to that in the system Ag-In, namely, the μ phase is related to the terminal α -phase in the same way that the α' -phase is related to the terminal α -phase in the system Ag-In.

In this case, the homogeneous fields of the μ -phase and the α' -phase in the respective binary systems would in all probability be joined in the ternary system as shown in the "Isothermal Sections". If the two phases have indeed the same crystal structure, they would have very similar cell edges, viz. $a = 4.114 \text{ \AA}$ for α' and $a = 4.051 \text{ \AA}$ for μ ; it would be expected that Al and In atoms are interchangeable in the two structures and this would result in a homogeneous field in the ternary system. To prove this point conclusively further work is required.

Other Aspects of the Ternary System

The two peritectic reaction-isotherms of 780°C and 695°C in the, Ag-Al, and Ag-In, systems respectively form a connecting reaction plane through the ternary system. This is evident from "Vertical Section I" Fig. 17. Similarly, the 610°C peritectoid isotherm of the binary Ag-Al, and the 670°C peritectoid isotherm of the Ag-In binary, form a connecting reaction plane through the ternary; and the 727°C isotherm of the binary Ag-Al and the 660°C isotherm of the binary Ag-In are similarly connected. This is again evident from Fig. 17. Thus the high temperature β -phase (bodycentred cubic) which exists in the binary systems Ag-In and Ag-Al respectively forms a connecting homogeneous volume through the ternary system. This is not surprising, since the β -phases of the two binary systems have the same crystal structure and the cell edges are comparable. viz.

at 648°C $a = 3.3682 \text{ \AA}$ (67) for β (Ag-In) i.e. Ag_3In

at 700°C $a = 3.3002 \text{ \AA}$ (12) for β (Ag-Al) i.e. Ag_3Al .

This means that the In and Al atoms are interchangeable on the lattice sites of the bodycentred cubic structure.

The three-phase equilibrium of the binary Ag-Al at 566°C (eutectic) terminates in the ternary on an invariant plane at 506°C , ("Vertical Section II", Fig. 18.). From "Vertical Section III" Fig. 19, it appears that an invariant plane also exists at 241°C . The binary three-phase equilibrium in the system Ag-In at 205°C probably terminates on this invariant plane.

Summary

A number of alloys strategically placed in composition in the ternary system were examined under the microscope. From these observations, the known contiguous binary systems, and application of the phase rule, a room temperature isothermal section was constructed. Three vertical sections through the ternary system were partially constructed from differential thermal analysis data. These data show that invariant planes occur in the system at 143°C , at 148°C , 241°C and 506°C . Isothermal sections were also constructed at 143°C and 148°C respectively, with the information obtained from the vertical sections and the room temperature isothermal section. The transformation at the 143°C invariant plane is a ternary eutectic, at 148°C a ternary peritectic of the second kind, and the other transformations at 241°C and 506°C are also ternary peritectics.

Some evidence indicates that the μ -phase of the binary system, Ag-Al, is a primitive cubic phase with a much smaller cell edge ($4.051 \text{ \AA}$) than previously found. No conclusive evidence could be obtained.

The high-temperature reaction isotherms of the binary systems Ag-In and Ag-Al, do not terminate on invariant planes, but form a connecting three-phase system.

The high-temperature β -phase of the binaries, Ag-Al, and Ag-In, form a connecting single-phase region in the ternary system. The conclusion is reached that Al and In atoms are interchangeable in the β -phases of

the two binary systems. Some evidence indicates that the ζ -phase of the Ag-Al system and the γ -phase of the Ag-In system also link up through the ternary system forming a single-phase region.

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