AN INVESTIGATION INTO THE SEPARATION OF SOLDERED CONNECTIONS FROM GOLD PLATED ELECTRONIC CIRCUIT BOARDS.

A dissertation submitted to the Faculty of Engineering, University of the Witwatersrand, in fulfillment of the requirements for the degree of Master of Science in Engineering, by J. D'A. Kirkman B.Sc. (Eng.)

This work was carried out in the Department of Metallurgy of the University of the Witwatersrand, under the supervision of Emeritus Professor D.D. Howat.

UNDERTAKING

I certify that this is my own work and has not been submitted for a Master of Science Degree at any other University.

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ABSTRACT

The unpredictable failure of soldered connections to gold plated printed circuit boards has caused widespread concern in the electronics industry as to the suitability of gold as a material for the protection of delicate circuitry from corrosion. Accordingly, this study was undertaken of the metallurgical reactions occurring between gold and lead-tin solder, and the effects of these reactions upon the integrity of soldered joints between gold surfaces.

The three aspects of the investigation were:

(a) A study of the effect of temperature upon the dissolution rate of gold in molten lead-tin solder.

(b) The identification of compounds which formed during soldering and ageing of the joints.

(c) The measurement of the shear strengths of soldered joints between both bulk gold and gold plated surfaces.

The dissolution rate of gold in molten solder was determined by dipping a weighed gold plate into a solder bath for a certain time, removing it and dissolving away the adherent solder in acid, prior to re-weighing the plate. Dissolution rate curves were obtained for various temperatures, and the method was extended to study the effect of small additions of nickel to the gold, to reduce the dissolution rate.

The compound identification was achieved by examination of the structures obtained when gold and solder and gold and pure tin were reacted together. Microscopic, X-ray diffraction and electron microprobe methods were used to distinguish between the various intermetallic compounds formed.

Soldered lap joints were constructed using bulk gold samples and gold plated surfaces typical of those used commercially. The shear strengths of the joints were measured and the fracture surfaces were

studied using optical and scanning electron microscopy. The variables studied were soldering temperature, time of ageing at 100°C after soldering, thickness and type of gold plate and the effect of nickel substrate.

The dissolution of fine gold in molten lead-tin solder was found to be rapid and extremely temperature dependent. The addition of five per cent nickel to the gold decreased the dissolution rate markedly. The three intermetallic compounds $AuSn_4$, $AuSn_2$ and AuSn formed during soldering, and a duplex $AuSn_4/AuSn_2$ layer was present at the gold/solder interface. Growth of the compounds was observed during ageing at 100°C after soldering.

The shear strengths of the solder lap joints decreased markedly on ageing at 100°C, due to growth of the intermetallic compounds in the joint. In the case of the gold plated joints, the presence of a thick gold plate and/or a nickel substrate decreased the strength of the joints. Soldering to gold plate from an acid cyanide bath resulted in unacceptably low strength joints.

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INTRODUCTION

The manufacture of electronic equipment accounts for a significant proportion of the gold used for industrial purposes. The rapid developments in this field over the last three decades have given rise to many applications for which gold, with its rather unique properties, is the only practical and economic material. Unfortunately this same rapid expansion has meant that practical considerations have been given primary emphasis, while the scientific aspects have been somewhat neglected. This investigation, under the sponsorship of the Chamber of Mines of South Africa as a part of the programme on the promotion of the industrial use of gold, has been carried out in an attempt to identify and explain the metallurgical causes of a phenomenon which is causing widespread dissatisfaction with the use of gold in the manufacture of printed circuit boards.

The properties of gold which are of importance in the electronics industry are its nobility, solderability, ease of deposition onto complex shapes, low contact resistance, good electrical and thermal conductivity and the protection it affords to the underlying metal when applied in very thin electrodeposited layers. The various uses to which it is put include edge connectors on printed circuit boards, thin film conductors, sliding contacts, beam leads, substrates to which silicon and germanium semiconductors can be soldered directly and gold-plated printed circuit boards.

A printed circuit consists basically of a metallic network to which the various devices comprising the circuit are attached by soldered leads. While copper is normally used, a wide range of metals, such as iron and nickel, can be employed. Soldering to this metal substrate is difficult, requiring powerful fluxes which are difficult to remove completely and are highly corrosive. For this reason a gold layer is

plated onto the substrate in order to give a non-tarnishing, easily solderable surface which can be stored for long periods before construction of the circuit. A lead/tin solder of eutectic composition is normally used and because gold is readily wetted by this material, a mild, non-corrosive resin flux can be employed. The circuits are finally assembled to produce a wide variety of electronic equipment, computers being the most common example.

Obviously, the reliability of the soldered connections is of extreme importance since most of the circuits are soldered automatically and many of the joints are so-called 'down-the-hole' joints where visual inspection is difficult. The circuits are tested before assembly but if the properties of the joint should deteriorate during operation of the computer, malfunctions which are costly and difficult to trace will occur. Many cases have arisen where soldered connections to gold-plated printed circuit boards, which have adequate strength immediately after soldering, are found to have separated under little or no applied stress after operating for several months, usually in an area of the computer where the ambient temperature is fairly high. While it was known that gold and tin react to form a series of intermetallic compounds, and that the presence of such compounds in a joint is normally detrimental to the strength of the joint, it was presumably thought that if the as-soldered strength was adequate, there would be no deterioration of the bond. Unfortunately, this was found not to be the case, and this led to the suggestion that certain metallurgical changes which reduce the joint strength were taking place, even though the operating temperature was relatively low. Accordingly, this investigation was undertaken in an attempt to determine the nature of these changes, and if possible to establish a procedure by which the embrittlement of soldered joints onto gold could be prevented or minimised. During the course of the

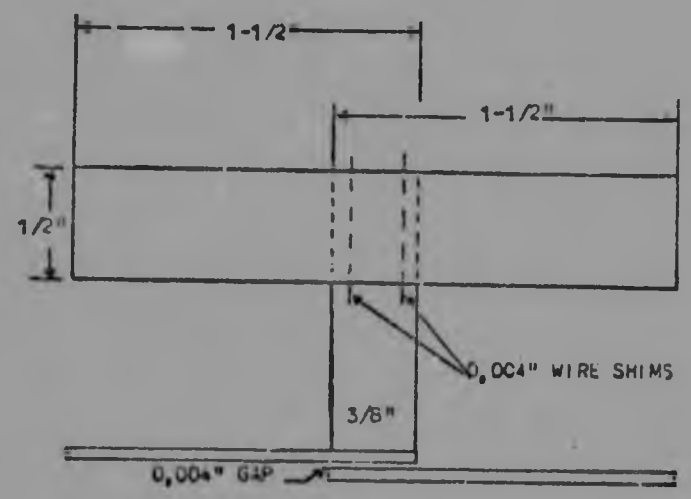
investigation, the following fields have been studied:

1. The kinetics of the dissolution of gold in molten lead/tin solder.
2. The identification of the various intermetallic compounds which form during soldering, and the correlation with the Au - Pb - Sn equilibrium diagram of the structures produced.
3. The growth of the intermetallic compounds during the ageing of joints at temperatures encountered in normal operation.
4. The tensile properties of gold-solder joints in both the as-soldered condition and after ageing for long periods.
5. The addition of alloying elements to the gold in order to reduce dissolution and the formation of intermetallic compounds.
6. The effect of the various different types of gold electroplate in commercial use.

2. LITERATURE SURVEY

2.1 Studies Relating to the Separation of Soldered Connections from Gold Plated Substrates

The first of these investigations was carried out in 1963 by Harding and Pressly[1]. The study covered both the weakness of soldered joints and the failure of solder to wet the gold plate. In the first case, soldered lap joints were made up between gold-plated copper panels as in the diagram below.



ASSEMBLED LAP SHEAR TEST SPECIMEN.

A study was made of the effects of gold-plating process, thickness of gold plate, soldering temperature and time at soldering temperature upon the shear strength of these joints. Thirteen types of gold plate were chosen, and these included pure gold (99,9%) and various alloy golds (containing Co, Ni or Ag) both with and without organic brighteners. Each type of gold plate was available in a range of thicknesses from 0,25 to 7,5 microns, and the joints were soldered at various temperatures in the range 188 to 288^{o}C. Soldering times were 5, 15 and 120 seconds and only solder of the eutectic composition (63% Sn, 37% Pb by weight) was used. After the shear strength of each joint had been determined, the

joints were examined microscopically to determine the metallurgical structure of the solder and the location and nature of the fracture. The results of this part of the investigation can be summarised as follows:

1. The shear strength varied widely, according to the type of gold plating, thickness of gold and soldering temperature.
2. The pure gold plates showed a marked decrease in strength with increasing gold thickness and soldering temperature.
3. An increase in soldering time produced a decrease in joint strength, although this effect was not as marked as in 2 above.
4. The alloy golds generally gave lower strengths than the pure gold plates, and the presence of organic brighteners had little or no effect.
5. Several of the alloy golds showed an initial decrease followed by an increase in strength as the soldering temperature increased.
6. Strong joints produced ductile, fine grained fracture surfaces, while weak joints exhibited a coarse, crystalline surface.
7. With the thicker alloy gold plates, a dewetting effect by which the solder initially spread over the gold, but then could not wet the gold/solder alloy formed, was apparent.
8. High gold thicknesses and soldering temperatures resulted in fractures at the solder/substrate interface.
9. Microscopic examination of the fractured joints revealed that at the lower plate thickness, all the gold dissolved to form white crystals in the solder, while at higher thicknesses some residual gold remained. In this case a white alloy layer was observed adjacent to the gold, with fine acicular crystals extending perpendicularly from this layer into the solder. The amount of gold which dissolved and then precipitated in the bulk of the solder as white

crystals of compound, was found to increase with soldering temperature.

The wettability of the various types of gold plate was studied by measuring the extent to which solder spread over a heated, fluxed, gold-plated test panel. It was found that all the gold deposits were superior to pure copper in this respect and that the pure gold deposits were somewhat more readily wetted than the alloy ones. The thin gold plates were slightly more readily wetted than the thick ones and it was noted that if the gold-plated panel was held at temperature for long enough, the solder would eventually draw back from the gold surface.

The following conclusions were reached by the investigators:

1. Thin, pure gold plate (less than 1,25 microns) and very thin, alloy gold plate (less than 0,25 microns) dissolve readily in lead-tin solder and do not weaken joints measurably.
2. Thick gold plate dissolves in the solder but decreases the strength of the joint.
3. A loss of strength will be caused by any factor which increases the amount of gold in the joint e.g. a thick gold plate, a high soldering temperature or a long soldering time.
4. Alloys of the Au - Sn - Pb System are weaker than eutectic lead-tin solder because of the formation of large, brittle, acicular crystals of $AuSn_4$ in the solder.
5. Alloy golds containing nickel, cobalt or silver undergo a phenomenon whereby the solder initially wets the gold but then draws back leaving ridges on the surface.

Finally it was recommended that thick gold plating should be avoided when strength is important, that pure gold plate should be selected and that the soldering operation should be closely controlled to minimise soldering time and temperature.

While the above investigation constitutes a valuable and comprehensive study, it is felt that certain aspects of the problem were neglected.

No attempt was made to identify the various intermetallic compounds formed in the joint and no work was done on the effect of ageing the joints at temperatures typical of those encountered during operation in a computer, for example. The recommendation that the gold layer be kept very thin is of doubtful value, since diffusion of the substrate material to the surface can occur during storage before soldering, thus reducing the solderability of the gold plate.

Foster[2] was another of the early investigators in this field. He found that the reaction between gold plate and molten solder was almost instantaneous, dissolving the entire gold coating and forming a stiff, easily fractured alloy. Microscopic examination revealed white crystals and fractured needles of a brittle intermetallic compound. Alloys containing 5, 10 and 15% gold in tin and in lead were cast into elongated ingots and these were submitted to a bend test. The alloys containing 10 and 15% gold were all so brittle that they fractured with no apparent bending. Ternary alloys were then made up with 60% Sn - 40% Pb and gold in various proportions and tested as above. Once again the specimens containing 10 and 15% gold were completely brittle. Fracture was found to follow the edges of the white acicular crystals present in the alloy.

Lap joints were then made up with the Pb - Sn - Au alloys studied earlier. Maximum shear strength was reached at a gold concentration of 2½%, the strength decreasing rapidly thereafter and falling below that of a straight 60 - 40 solder joint when the gold content exceeded 5%. Foster therefore recommended that the gold be removed from the joint area before soldering gold-plated components.

Weil et al.[3] studied the spread of 60% Sn - 40% Pb solder on gold electrodeposited onto silver and nickel substrates. It was found that spreading was greatest at high temperatures and that the solder failed

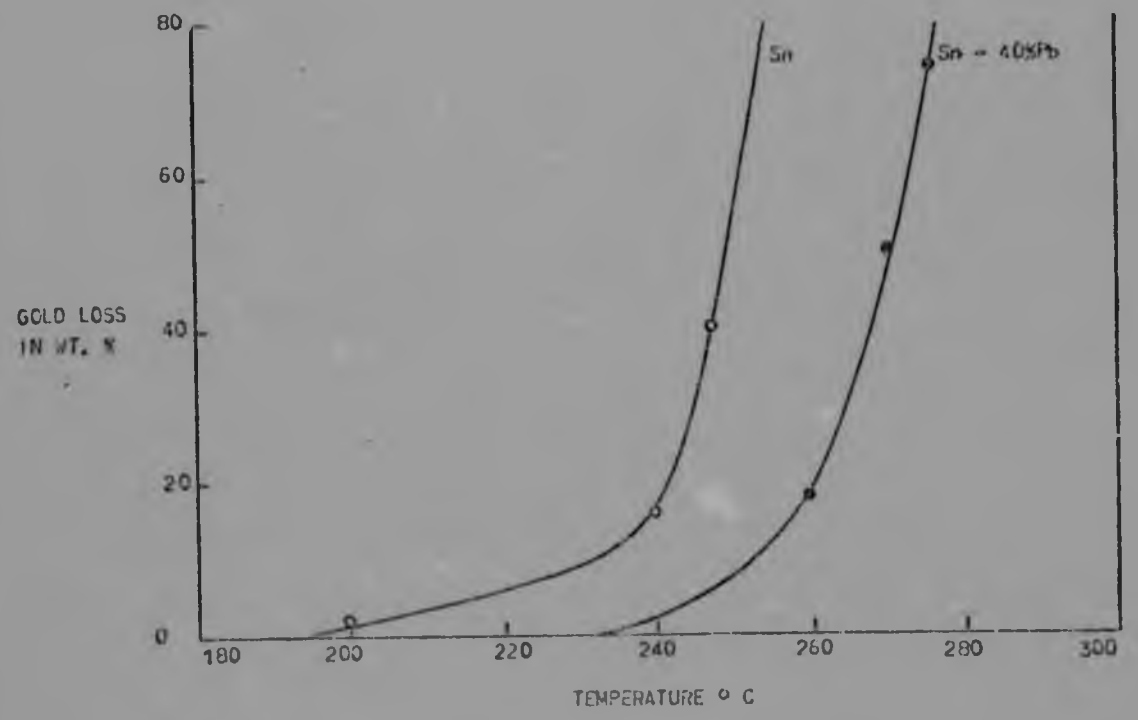
to wet the nickel substrate when the gold layer was dissolved away. The advancing solder front was found to contain a large proportion of intermetallic phase constituents. Spreading was found to be favoured on gold plates with surface capillaries (such as grain boundaries) as opposed to smooth, bright deposits.

The strengths of soldered joints were studied by soldering a pin onto a gold-plated sheet and measuring the force required to pull the pin away from the surface. The results showed no consistent correlation with either soldering temperature, type of gold deposit or substrate material. There was also no direct relationship between the ease of spreading and joint strength, and the use of different solders did not result in major variations in joint strengths.

Whitfield and Cubbin[4] suggested that two intermetallic compounds can form in soldered connections. These are $AuPb_2$ which is dendritic and $AuSn_4$ which is acicular, the compounds forming on cooling from temperatures above 215 and 217°C respectively. It was proposed that as a solder front moves across a gold-plated surface, the gold is dissolved and carried forward. The concentration of gold in the front increases until the solder becomes saturated, this being indicated by the appearance of a white alloy layer at the interface. Since this abnormal crystal formation was found to be confined to the leading edge of the solder fillet, the embrittling effect was small in the case under study, which was the soldering of gold-plated wires to gold-plated springs. It was noted, however, that when two gold surfaces are soldered together, high concentrations of gold can be trapped in the joint, giving rise to embrittlement.

Harmsen and Meyer[5] investigated the embrittlement of soldered joints to gold plated substrates and the poor spreading of solder on gold surfaces by means of dipping tests with different solders. The unusually

fast dissolution of gold in soldering alloys was considered responsible for the difficulties encountered. The graph below shows the effects of temperature upon the solubility of gold in tin and a 60% Sn - 40% Pb solder.



Thwai es[6] has provided a review of the various methods for assessing the solderability of various solder-flux-base metal systems. The majority of investigators have used area of spread tests but it is clear that any one test will not suffice to provide a quantitative measure of solderability for all systems. It has been found from practical experience, confirmed by experiment, that of the lead/tin alloys, the eutectic composition has the best properties.

A comprehensive study by Bader[7] of the dissolution of gold, silver, palladium, platinum, copper and nickel in molten 60% Sn - 40% Pb solder led to the conclusion that palladium, copper, silver and gold are unsuitable for thin film applications. Over the range 200 - 480°C, the temperature dependence of the dissolution rates was found to follow Arrhenius behaviour i.e.

rate of dissolution $r = Ae^{-B/T}$

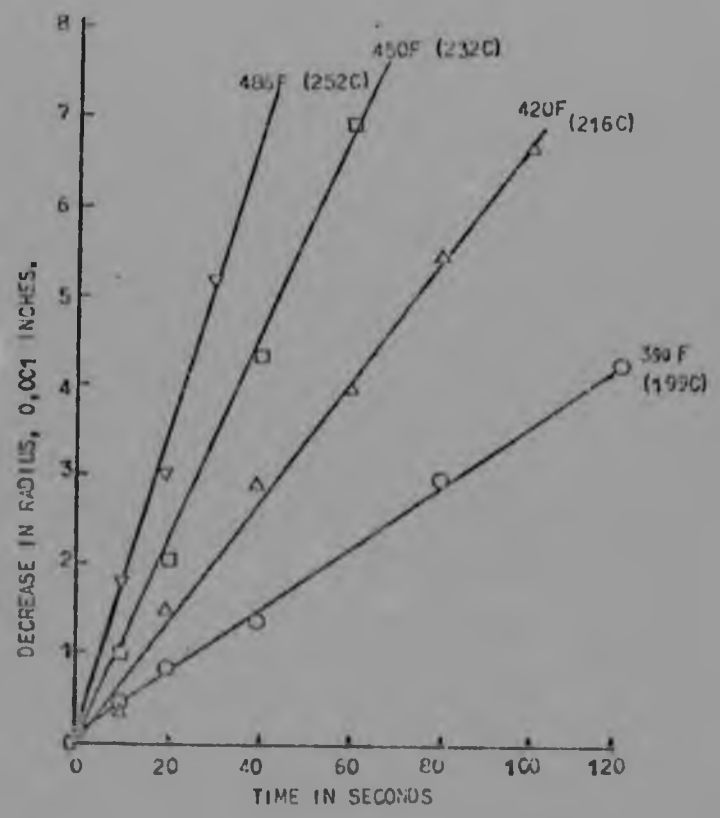
where A and B are constants, and T is the absolute temperature. From the above equation:

$$\log r = \log A - \frac{B}{T}$$

A plot of log r against 1/T was found to yield a straight line of slope B, and intercept log A in the case of all the metals studied.

Gold and silver were found to have the highest dissolution rates of the metals studied, while platinum and nickel had the lowest. Gold is classed as a "soldered-through" protective coating, since it dissolves in the solder and the metallurgical bond is formed with the basis metal. The formation of intermetallic compounds by reaction of the dissolved gold with the solder causes embrittlement.

At the temperatures studied, gold reacts with the tin in the molten solder to form solid intermetallic compounds. This incongruent dissolution introduces many variables into the kinetics of the process and therefore no theoretical significance can be attached to the values of A and B obtained. For this reason a practical method consisting of dipping a gold wire into a bath of molten solder for a set time, removing it and measuring the decrease in diameter of the wire microscopically was adopted. The results obtained are shown on the graph below:



DISSOLUTION OF GOLD WIRES IN MOLTEN 60Sn-40Pb SOLDER

Linear plots were obtained at each temperature and the slope of each line gives the dissolution rate at that temperature. Possible rate controlling processes for the dissolution reaction are diffusion in the metal, diffusion through the intermetallic compound layer, and transport in the liquid phase.

Microscopic examination of the gold wires after reaction revealed a compound layer at the metal/solder interface, which was believed to be $AuSn_4$. Above 252°C (486°F) extremely rapid dissolution was found to occur, and this was thought to be due to the peritectic decomposition of $AuSn_4$ to form $AuSn_2$ above this temperature. A different compound, thought to be $AuSn_2$ was formed at 278°C (500°F).

Brewer[8] studied the use of various types of solder with gold-plating. Some solders were found to increase in strength with gold pick-up, others to decrease. High temperature soldering of gold with lead-tin

solders gave very weak joints, but good results could be obtained if soldering time and temperature were held to a minimum, in order to prevent excess alloying with the gold. In cases where this is not possible a 90% In - 10% Ag or an 80% Au - 20% Sn solder may be more suitable. These solders do not however compare well with the lead-tin eutectic as regards wettability or low melting point.

Cavanagh and Longan[9], in a survey of the solderability of protective coatings classified gold as a soluble coating since it dissolves on soldering and the final connection is to the basis metal. The dissolution rate is dependent upon the solubility of gold in the solder used, the thickness of the deposit and the time and temperature of soldering. The embrittlement of soldered joints to gold was attributed to $AuSn_4$ formed at the interface.

The malfunction of a Saturn V launch checkout computer system initiated a study of solder-circuitry separation problems by the National Aeronautics and Space Administration in the United States[10]. The failure was traced to an intermittent soldered connection on a computer module board. Investigation of additional connections to this board and to boards from other computer systems revealed similar widespread solder-circuitry separations. Boards which exhibited this problem were double-sided circuitry plated with copper that contained brightener additives and overplated with acid cyanide gold containing cobalt. The circuit sides of the board were wave soldered and the component sides were hand soldered. Both sides, including the plated through holes, exhibited solder separation. The polyurethane coating in the areas affected showed severe discolouration, caused by high operating temperatures, but nongold-plated boards which also showed this discolouration revealed no loss of joint strength. Thus it was apparent that heat, coupled with time, was not the only factor causing the solder-circuitry

separations. Normal operating temperatures in the computer were found to reach 90°C in certain areas, but it was considered that the severe discolouration of the polyurethane coating was caused by even higher temperatures. The only visual indication of joint failure was a darkening of the gold plate adjacent to the solder fillet. No separation was observed on circuit boards which had been tinned rather than gold plated, but failures were found on boards which have been plated with copper containing brightener additives. Boards plated with copper from a pyrophosphate bath containing no brighteners did not suffer from separation.

The strengths of various connections were tested by either pushing or pulling the lead until it came away from the board. The results varied widely, but generally those connections which showed signs of separation were weaker than those in areas of the board which had not been subjected to high temperatures. Microscopic examination revealed that separation in the weak joints was uniform and occurred at the copper/solder interface. Acicular crystals were found dispersed throughout the solder mass and a gold-tin intermetallic compound layer was present at the interface. Separation occurred between the gold plate and this layer, or if the gold had all reacted with the solder, between the copper substrate and the compound layer.

A laboratory study was then initiated to study the effects of gold plating upon joint strength. Three substrates were used, namely bare copper, copper overplated with a 6,4 micron layer of hard gold, and copper from which the gold plate had been removed in the areas to be soldered. A large number of leads were soldered to boards of the above three types and the connections were tested periodically while the boards were aged at 100°C. Previous investigations had shown that gold plating had no deleterious effects over five years at temperatures below 70°C.

The solder - to - gold connections showed a significant strength degradation after only 166 hours at 100°C. Progressively weaker and more erratic strengths were measured until termination of the test after 2230 hours. The connections to both the copper and erased gold boards remained approximately constant in strength. A minimum push strength of 0,91 kg. was obtained with gold over copper, as compared with 4,99 kg. for the other two types. No separation at the solder/copper interface occurred with the bare copper and erased gold boards, while partial separation at this interface occurred after 166 hours with the gold plated board. This increased until complete separation was observed after 1054 hours.

The connections to the gold plated board were grainy, dull grey and porous, as opposed to the shiny, smooth appearance of those of the other two types. Metallographic examination showed porosity due to the outgassing of organic materials in all the solder - to - gold connections. The solder - to - copper joints revealed no separation even though a copper-tin intermetallic compound formed and was observed to increase in thickness during the ageing treatment. After completion of the test it was found that the gold plating away from areas which had been soldered was still acceptably bonded to the copper substrate.

Using a technique developed by Munier[11], the author isolated a transparent organic polymer from samples of gold plate from areas which had been soldered to and other areas which had not. It was concluded that elevated temperature will, in time, concentrate this codeposited polymer at the solder-circuitry interface as a transparent film.

The final recommendations were that copper plating solutions containing brighteners and other organic additives, and cyanide gold plating solutions be suspended from future printed circuit board fabrication processes. When gold plating is mandatory, non cyanide gold should be

specified and it should be removed prior to soldering. The recommendation to avoid the use of gold plate wherever possible was also made by the United Kingdom Department of Trade and Industry[12].

The work of Munier[11] has shown the polymer to be in the form of a clear, transparent film deposited alternately with the gold and existing as well-defined layers covering the entire cathode area. It must therefore be either considerably porous or electrically conducting. Further work on the inclusion of polymer in electrodeposited gold[13, 14, 15] has shown that polymer is present in all golds from acid cyanide solutions. Polymer concentration is dependent upon cathode efficiency and the presence of added metals capable of forming a low-pH-stable complex. The amount of carbon deposited in the form of polymer may exceed 1% by weight.

Davis[16] identified an organic polymer in gold from an alkaline cyanide bath and found this gold to have poor solderability. Plate from a bath containing no free cyanide revealed no polymer and soldered readily. It was therefore concluded that poor solderability was attributable solely to the presence of polymer in the gold plate. Plating of components in cyanide baths was not recommended when solderability was a requirement.

Lloyd and Groenewald[17] challenge the assumption that the polymer is responsible for the separation of soldered connections, giving the following reasons:

1. The polymer is disseminated throughout the gold plate, but separation occurs mainly at the gold plate/copper interface.
2. The polymer would probably be destroyed by the high temperatures experienced during soldering. The porosity noted in the soldered joints may be due to gas evolved during the destruction of the polymer.

3. The presence of a polymer would not really explain why thick gold plate is more prone to failure than thin plate.
4. Only trace quantities of polymer are present (ca. 0,3% C), but macro quantities of high-molecular-weight rosins are also present during soldering, which would be expected to have a far greater deleterious effect were such substances to be implicated in separation.
5. Most of the gold reacts to form gold-tin compounds and expulsion of any polymer during the formation of such alloys would be expected.

A further reason to doubt this assumption is that no separation was found in gold-plated areas which had not been soldered to, even after ageing at 100°C for over 2 000 hours. It is also difficult to envisage a mechanism whereby an organic polymer in the form of a thin sheet could diffuse through a dense layer of gold to concentrate at the gold/copper interface.

Ainsworth[18] attributed the embrittlement of soldered joints on gold to the presence of $AuSn_4$ which forms as a continuous layer at the solder/gold interface and as needles in the bulk of the solder fillet. A thick gold deposit and high soldering temperatures favour this effect. The solubility of gold in lead-tin solder can be reduced by adding silver or cadmium to the solder, but no data is available on the mechanical properties of these joints. Embrittlement is greatly reduced by the use of lead - tin - indium and lead - tin - indium - zinc solders, which have lower melting points than a 60% tin - 40% lead solder, due to the lower soldering temperature and the preferential formation of $AuIn_2$ at the interface. However, these solders are expensive and give lower joint strengths than those possible with 60 - 40 tin-lead solder.

It is recommended by Ainsworth that gold plating thickness should be kept below 1,5 microns to ensure freedom from embrittlement. These boards, however, should not be stored for long periods as the soldera-

ability will deteriorate due to oxidation or corrosion of the basis metal through pores in the coating. Where thick gold deposits must be used, it is necessary to remove the gold before soldering. The time and temperature of the soldering operation should also be kept to a min. um.

Lee[19] claimed that the use of an 85% Au - 15% Ni alloy electrodeposit instead of the normal hard, bright gold plate would prevent joint embrittlement. It was shown that the incorporation of nickel in the gold plate prevented dissolution of the gold during the soldering process and also stopped the diffusion of gold to react with tin during subsequent ageing at 110°C. Lee's findings were that a pure gold wire partially dissolved in molten solder to form an annular layer of gold-tin intermetallic compound and that this layer grew considerably during ageing, while a nickel/gold alloy wire did not react at all. Good solderability and corrosion resistance were claimed for the alloy.

The shear strengths of lap joints made up with gold plate and with Au - Ni alloy plate were also studied. In both cases, the specimens were prepared with and without a nickel undercoat. The soldering temperature was held constant and the thickness of the plate was increased up to a maximum of 5 microns. The shear strengths of soldered joints to the Au - Ni alloy plate, both with and without a nickel undercoat, were uniformly high, only decreasing slightly at high thicknesses. The gold plate without a nickel underplate gave the same strengths as the alloy plate up to a thickness of 0,65 microns, after which a steady decrease was observed. The gold plate with a nickel underplate gave weak joints, due to the fact that the gold dissolved and soldering was to the nickel substrate which had poor solderability. It was therefore recommended that no nickel underplate be used with a soluble coating such as gold. The addition of 15% nickel makes the gold insoluble in

solder, thus avoiding this problem.

Recent work on reducing porosity in thin gold electrodeposits[20] has shown that a combination of electropolishing prior to plating and ultrasonic agitation during plating can achieve a consistently low residual porosity in gold coatings as thin as 2 microns.

In a critical review of soldering to gold surfaces, Thwaites[21] considers both the solderability of gold coatings and the metallurgical reactions that occur during soldering. It is concluded that the solderability of pure gold is excellent, but that of the hard, bright electrodeposits commonly used is strongly dependent upon the metallic alloying additions and the organic additives used. Included carbonaceous material decomposes on soldering to cause gross gas porosity in the joint. Some alloy deposits cause the solder to spread unevenly and solidify with a rough surface.

With regard to the strength of soldered joints, rapid solution of gold coatings and intermetallic compound formation occur in molten solder. Joint strength and ductility are low if more than about 4 per cent gold is present in the solder in the joint. When residual gold is present, joints are always weak, due to the formation of massive layers of the intermetallic compound $AuSn_4$. Up to the date of writing, no new solders had been devised to overcome this problem, with the possible exception of an expensive indium-rich alloy.

The following alternatives are suggested for producing sound soldered joints to a gold surface:

1. Use a gold - 15% Ni plate which reacts too slowly with molten solder to produce intermetallic compounds.
2. Limit the gold thickness to about 1 micron (preferably pure gold) and use a tin/nickel undercoat to protect the substrate.
3. Remove the gold plate from areas where soldered joints are to be made.

2.2 PHASE EQUILIBRIA IN THE BINARY SYSTEMS Pb-Sn, Sn-Au AND Au-Pb

2.2.1 The Pb-Sn System[22]

Lead and tin form a simple eutectic system, shown in Figure (1). The eutectic temperature is 183°C and the composition 38,1 weight per cent lead. The (Sn) phase can contain 2,5 wt.% lead at the eutectic temperature, but room temperature solubility is low (less than 0,3 wt.%). The (Pb) phase has a maximum solubility of tin of 19 wt.% at the eutectic temperature, and a room temperature solubility of 2,9 wt.%.

2.2.2 The Sn-Au System[22, 23]

The phase diagram for this system is shown in Figure (2). Three intermediate phases AuSn (37,57 wt.% Sn), $AuSn_2$ (54,62 wt.% Sn), and $AuSn_4$ (70,65 wt.% Sn) are formed, with a further gold-rich phase forming between 12 and 16 atomic per cent tin. The $AuSn_4$ - Sn eutectic lies at 90,5 wt.% Sn and 214°C, and the solid solubility of gold in tin at 200°C is approximately 0,3 wt.%. AuSn has an ordered hexagonal structure of the NiAs type; $AuSn_2$ is orthorhombic of the $CoGe_2$ type; $AuSn_4$ has an ordered orthorhombic structure isotypic with $PtSn_4$ and $PdSn_4$, containing 20 atoms per unit cell. Both $AuSn_2$ and $AuSn_4$ exhibit very narrow ranges of homogeneity.

2.2.3 The Au-Pb System[22]

Until recently, the phase diagram shown in Figure (3) was accepted for the lead-gold system. Two intermediate phases Au_2Pb (34,44 wt.% Pb) and $AuPb_2$ (67,76 wt.% Pb) were known with Au_2Pb decomposing into Au and $AuPb_2$ on cold working, indicating that Au_2Pb is unstable below some undetermined temperature. Recently, however, a third gold-lead compound, $AuPb_3$, has been discovered[24]. This compound, which has a tetragonal crystal structure, had previously been reported in very thin evaporated gold-lead films but its presence in massive form had been doubted. A revised equilibrium diagram (Figure (4)) has since been published by

FIGURE 1 The Pb - Sn Equilibrium Diagram

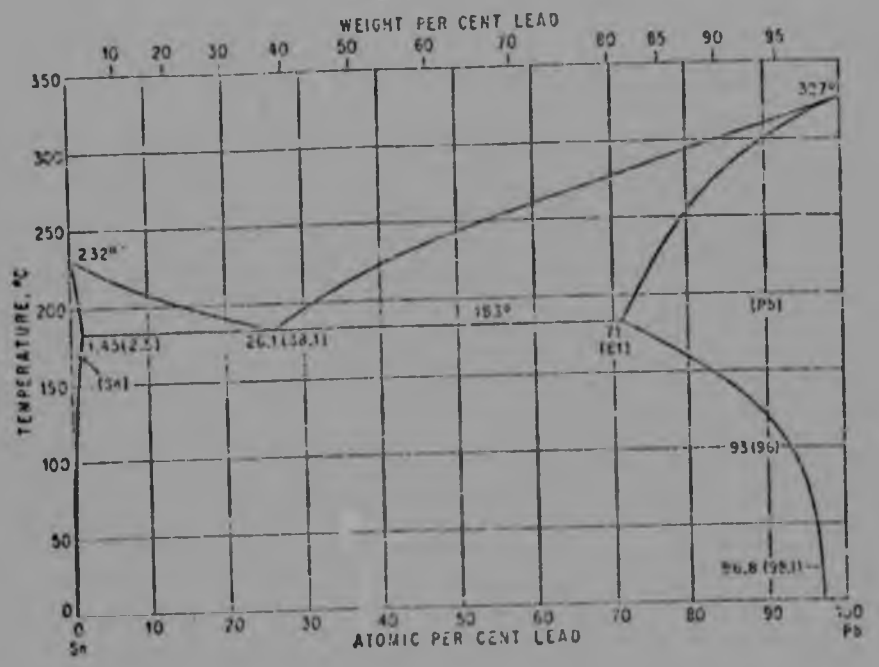


FIGURE 2 The Sn - Au Equilibrium Diagram

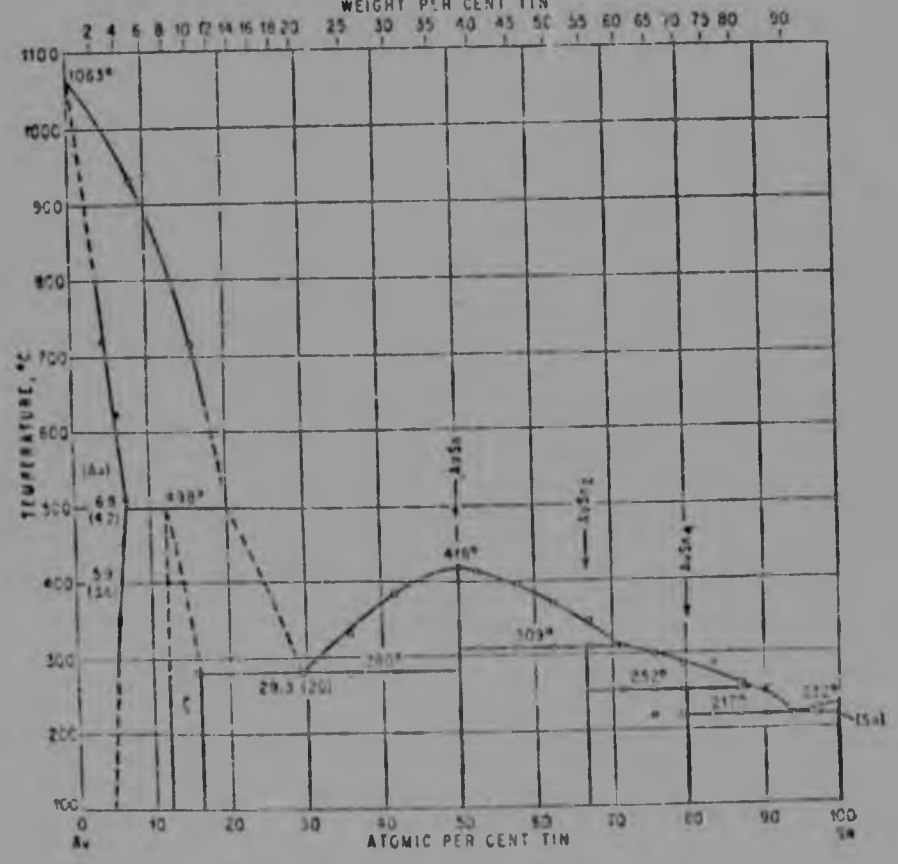


FIGURE 3 The Original Au - Pb Equilibrium Diagram

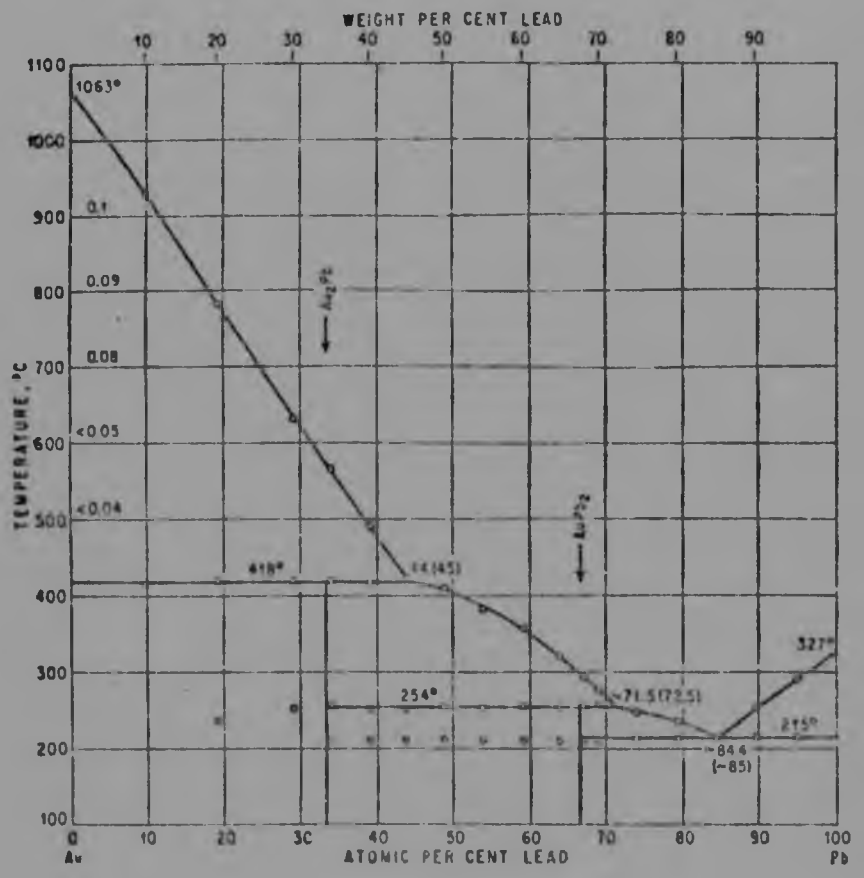
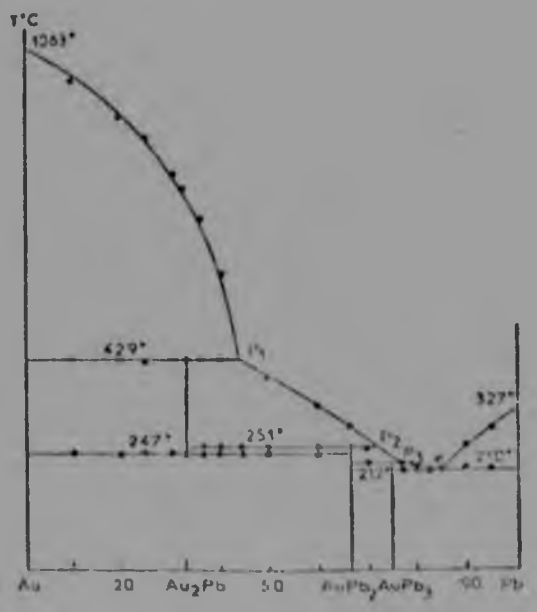


FIGURE 4 The Revised Au - Pb Diagram



Legendre and Souleau[25], showing the presence of the non-congruent compound, $AuPb_3$, and indicating the instability of Au_2Pb at low temperatures.

The solid solubilities of gold in lead, and of lead in gold are both extremely low, the solid solubility of gold in lead being 0,08 atomic per cent at 200°C.

V.d. Broek and Staats[26] studied interstitial dissolution and compound formation in the Au-Pb system. It was found that the crystal lattice of lead expands upon the dissolution of gold, although lead atoms are much smaller than gold atoms - this was in accordance with the idea that gold atoms occupy interstitial positions in the lead lattice.

The compound $AuPb_3$ was formed by the reactions:

Peritectic at 222°C $\quad L + AuPb_2 = AuPb_3$

Eutectic at 212°C $\quad L = AuPb_3 + Pb$

The formation of $AuPb_3$ could be suppressed by quenching, when a metastable eutectic reaction:

$$L = AuPb_2 + Pb$$

occurred at only 0,5°C below the temperature of the stable eutectic. Au_2Pb was found to be stable from its peritectic formation temperature to as low as 200°C.

2.3 PHASE EQUILIBRIA IN THE TERNARY SYSTEM Au - Sn - Pb

As a result of interest expressed in the reactions of gold with molten lead-tin solder, Prince[27, 28] established the constitution of the AuSn - Pb - Sn partial-ternary system. AuSn, being a congruently-melting compound, enables the Au - Sn - Pb system to be split into two sub-systems Au - AuSn - Pb and AuSn - Pb - Sn. Since it is unlikely that gold concentrations in soldered joints will reach 50 atomic per cent, only the latter system is of interest in this study.

In order to investigate this field, it was first necessary to establish the quasi-binary AuSn - Pb section[27]. Thermal analysis and metallographic techniques established this to be of the eutectic type (Figure (5)), with the quasi-binary eutectic occurring at 292°C and 92 wt.% Pb. The solubility of AuSn in lead was found to be less than 1 wt.% at the eutectic temperature. Assuming the absence of ternary compounds, the equilibra in the partial ternary system were predicted to be as in Figure (6).

With a knowledge of the AuSn - Pb quasi-binary system, the AuSn - Pb - Sn ternary could be investigated[28]. The projected liquidus surface obtained is shown in Figure (7). The eutectic valley originating at the AuSn - Pb eutectic point e_3 descends to meet the peritectic fold emanating from the binary peritectic reaction:

$$liq + AuSn = AuSn_2$$

At this point P_1, a ternary quasi-peritectic reaction occurs:

$$liq + AuSn = Pb + AuSn_2 \qquad 275^{\circ}C.$$

From P_1, the liquid deposits a mixture of Pb and $AuSn_2$ until point P_2 is reached when a second ternary quasi-peritectic reaction occurs:

$$liq + AuSn_2 = Pb + AuSn_4 \qquad 208^{\circ}C.$$

From P_2 the liquid deposits a mixture of Pb and $AuSn_4$ until the ternary eutectic point is reached at E:

FIGURE 5 The Quasi-Binary AuSn - Pb Diagram

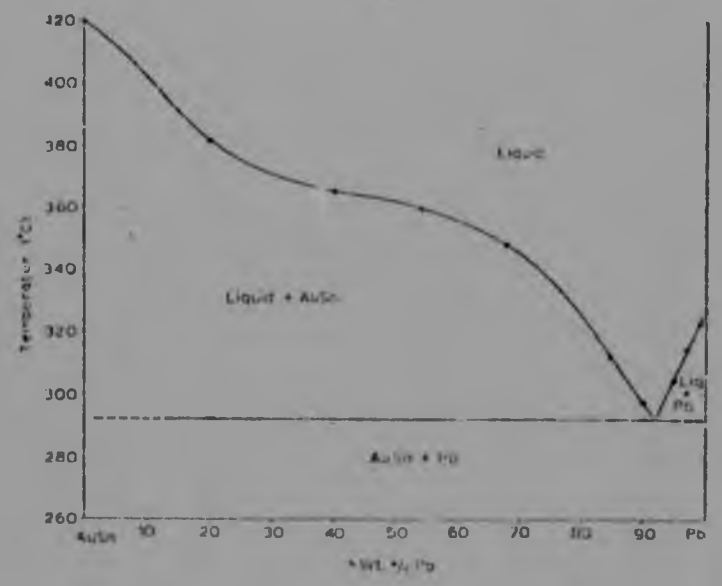
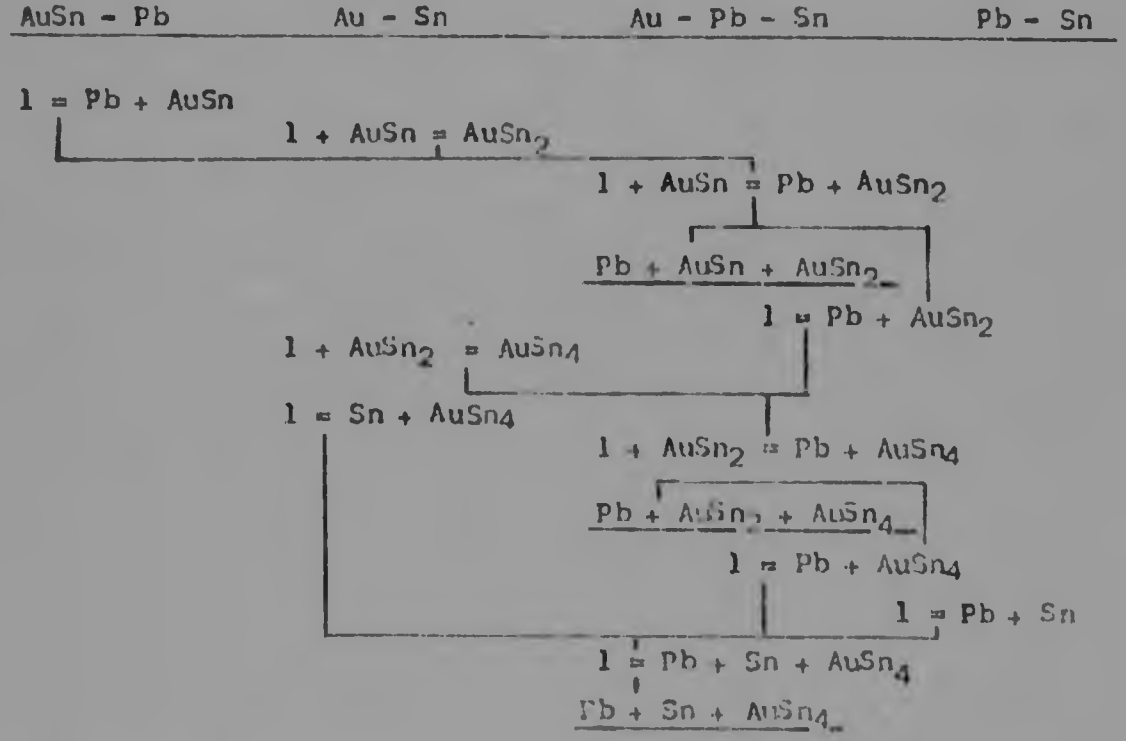


FIGURE 6 (Note: The Equilibria underlined are stable to room temperature). Phase Equilibria for the System AuSn - Pb - Sn.



$$liq = Pb + Sn + AuSn_4 \qquad 177^{o}C.$$

It should be noted that no Au - Pb compounds occur in soft-soldered joints to gold plated surfaces. The separation of lead from the ternary eutectic may be degenerate, giving rise to dendritic lead which may have been mistaken by earlier workers for dendritic $AuPb_2$.

Microscopic work confirmed the peritectic nature of the reactions at P_1 and P_2. Duplex grains were obtained, with an inner core of primary AuSn in the case of the reaction of P_1, surrounded by a peritectic rim of $AuSn_2$, and of primary $AuSn_2$ with a rim of $AuSn_4$ in the case of P_2.

The solubility of gold in a 60% tin - 40% lead solder was measured as 11% at 225°C, 17% at 250°C and 24% at 275°C.

Karnowsky and Rosenzweig[29] derived the ternary Au - Sn - Pb equilibrium diagram, which is characterised by the persistence of the congruently melting phase AuSn across the diagram to the lead corner. A tentative liquidus projection, shown in Figure (8), was obtained. This agrees well with that obtained by Prince for the AuSn - Pb - Sn system. There are seven isothermal reactions in the diagram since according to the phase rule, when four phases exist in equilibrium in a ternary system, the temperature must remain constant. With reference to Figure (8) they are:

1. $L + Au = Zeta + Au_2Pb$ 363°C
2. $L + Zeta = Au_2Pb + AuSn$ 247°C
3. $Au_2Pb + L = AuSn + AuPb_2$ 225°C
4. $L = AuSn + AuPb_2 + Pb$ 204°C
5. $L + AuSn = Pb + AuSn_2$ 277°C (275°C)
6. $L + AuSn_2 = Pb + AuSn_4$ 205°C (208°C)
7. $L = AuSn_4 + Pb + Sn$ 176°C (177°C)

The temperatures given in parentheses are those obtained by Prince.

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The temperatures given in parentheses are those obtained by Prince.

FIGURE 7 The Projected Liquidus Surface for the System AuSn - Pb - Sn (according to Prince[28]).

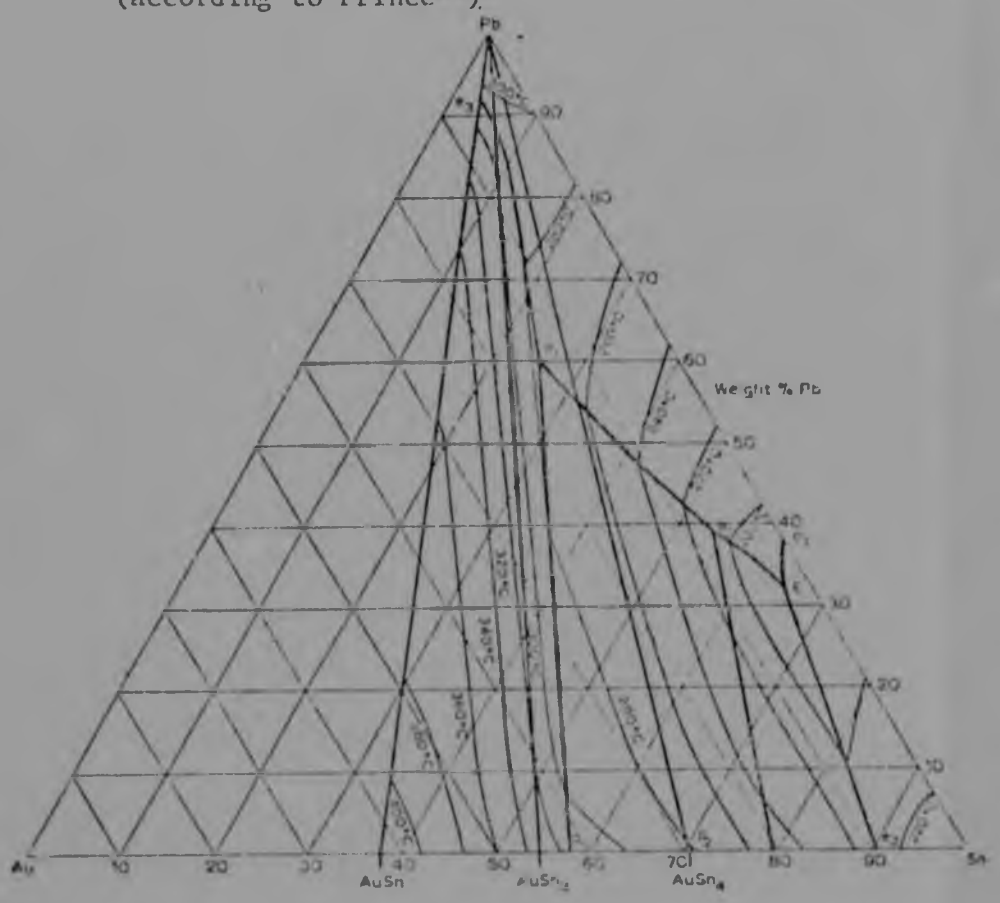
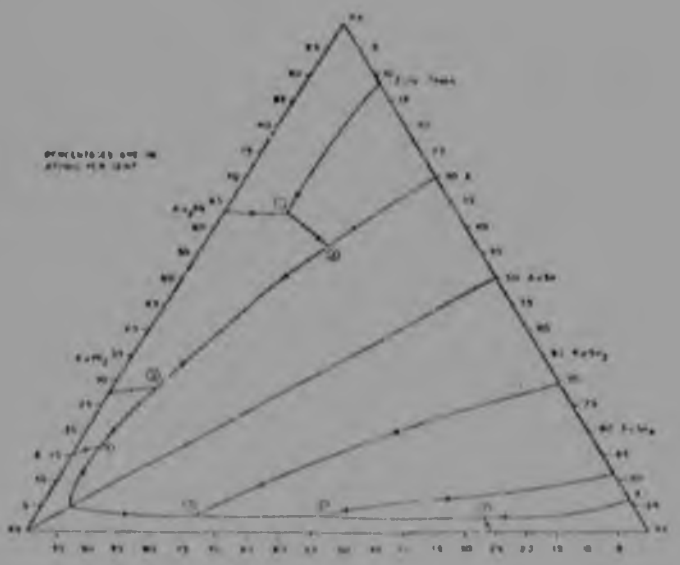


FIGURE 8 The Projected Liquidus Surface for the System Au - Pb - Sn (According to Kamowsky and Rosenzweig[29]).

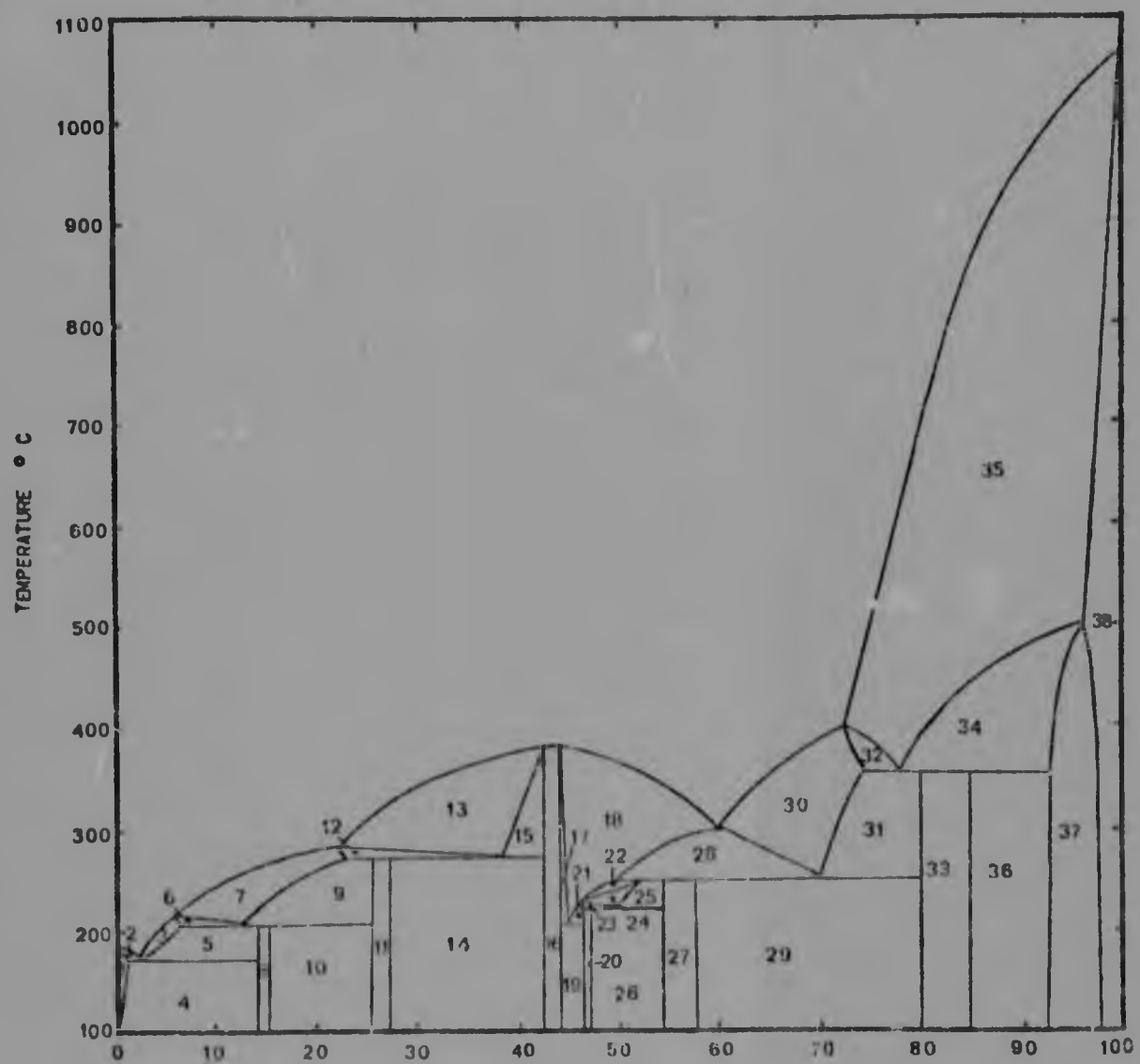


Thus there are two different paths that can be followed on cooling, depending upon the original composition of the melt. Unless the gold content of a soldered joint exceeds 50 atomic per cent, which is unlikely, lead will not form any compounds with the gold but will merely act as a diluent in the system.

A vertical section through the Au - Sn - Pb system from the eutectic solder composition to the Au corner was derived and is shown in Figure (9) Many deductions were made in the construction of this plot, especially since five of the seven reactions are of the peritectic type. Peritectic reactions are known to attain equilibrium with difficulty, and therefore the composition limits may extend further than those shown by differential thermal analysis.

It is interesting to note that the same compounds AuSn, $AuSn_2$ and $AuSn_4$ are found in the Au - Sn - Ag system[30], and that they form by similar ternary quasi-peritectic reactions, followed by a ternary eutectic reaction.

FIGURE 9 A Vertical Section Through the Au - Sn - Pb section from the Eutectic Solder Composition to the Au Corner.



Legend

1. Sn + Pb
2. L + Pb
3. L + $AuSn_4$
4. Sn + Pb + $AuSn_4$
5. L + Pb + $AuSn_4$
6. L + $AuSn_4$ + $AuSn_2$
7. L + $AuSn_2$
8. $AuSn_4$ + Pb
9. $AuSn_2$ + Pb + t
10. $AuSn_4$ + $AuSn_2$ + Pb
11. $AuSn_4$ + Pb
12. L + $AuSn_2$ + AuSn
13. L + AuSn
14. $AuSn_2$ + AuSn + Pb
15. L + AuSn + Pb
16. AuSn + Pb
17. AuSn + Pb + t
18. t + AuSn
19. AuSn + Pb + $AuPb_2$
20. $AuPb_2$ + AuSn
21. L + AuSn + $AuPb_2$
22. L + AuSn + Au_2Pb
23. L + AuSn + $AuPb_2$
24. AuSn + Au_2Pb
25. AuSn + $AuPb_2$ + Au_2Pb
26. AuSn + $AuPb_2$ + Au_2Pb
27. $AuPb_2$ + AuSn
28. L + AuSn + Zeta
29. $AuPb_2$ + AuSn + Zeta
30. L + Zeta
31. L + Zeta + AuSn
32. L + Au_2Pb + Au
33. Zeta + Au_2Pb
34. L + Zeta + Au
35. L + Au
36. Zeta + Au_2Pb + Au
37. Zeta + Au
38. Au

2.4 DIFFUSION AND SOLID-STATE REACTIONS IN THE Au - Sn - Pb SYSTEM

The findings by Pasciak[10] that soldered joints to gold plate deteriorated in strength after operating at elevated temperatures, and by Lee[19] that gold/tin compounds which formed on soldering grew during ageing at 110°C, suggest that diffusion-controlled reactions take place in the solid state at these relatively low temperatures.

It is well known that gold diffuses very rapidly in lead. The diffusion of gold in lead at room temperature was first studied by Roberts-Austen in 1896[31]. Gold in lead meets the requirements for rapid diffusion in that the solubility is very slight and the melting point of the solvent is low. Gold atoms are also very much smaller than lead atoms. A small amount of gold goes into substitutional solid solution in lead, but diffusion is by an interstitial mechanism. As a consequence of this the diffusion of gold atoms out of their positions in the lead lattice produces vacancies and the rate of further diffusion decreases. This was confirmed by Rossolimo and Turnbull[32].

Warburton[33] confirmed experimentally that the diffusivity of gold in lead decreases with increasing gold concentration. A model was suggested wherein gold diffusion is controlled at low temperatures and high concentrations by the motion of defects consisting of pairs of gold atoms, possibly a split interstitial. This casts doubt on the conclusion that diffusion of gold in lead is primarily due to the motion of conventional interstitials at any temperature or concentration.

Hooyer and Meijering[34] found that when a gold foil was clamped in close contact with a lead cylinder, compound formation at the gold/lead interface became apparent after some time. Only the compounds $AuPb_2$ and $AuPb_3$ were formed, the thermodynamically stable Au_2Pb being absent. This was apparently due to difficulty of nucleation of the Laves phase Au_2Pb, even at 200°C.

A similar phenomenon has been found in the diffusion behaviour of copper and gold[35]. When gold and copper were diffused together, only the phases Cu_3Au and $CuAu_3$, in an abruptly layered structure, were obtained. The ordered phase CuAu was conspicuously absent and the lack of any concentration gradient in the terminal metals was also noted. Both of these phenomena are contrary to the established laws of intermetallic diffusion. It was concluded that the compound growth rate must be controlled by atomic movements taking place at the interface in such a way as to ensure both the correct order and stoichiometry.

Herzig and Heumann[36] studied the diffusion of tin and gold in gold-rich gold-tin solid solutions. The self-diffusion of tin and gold were found to increase strongly with increasing impurity content.

Misra et al.[37] studied compound formation in the Au - Sn system. The heats of formation of AuSn, $AuSn_2$ and $AuSn_4$ at 273°K were found to be -3,65, -3,38 and -1,85 kcal/g. atom respectively. The solidus temperatures of the three compounds also decrease in the same order, indicating their relative stabilities. The free energy of formation of AuSn was given as below:

ΔF^{o} [0,5 Au(s) + 0,5 Sn(s) = 0,5 AuSn(s), 298°K] = -3,81 kcal/g. atom.

ΔF^{o} [0,5 Au(s) + 0,5 Sn(l) = 0,5 AuSn(s,l) 692°K(m.pt.)]

= -2,93 kcal/g. atom.

The compounds formed have essentially metallic and covalent bonding, the ionic contribution being low. This is confirmed by the low melting points or peritectic decomposition temperatures of the compounds and their low heats of formation. The nickel arsenide structure of AuSn has a low c/a ratio of 1,278, indicating a low value of the Madelung constant and hence predominantly metallic bonding.

In applications involving thin gold films carrying high current, electromigration may replace diffusion as the dominant method of mass

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In applications involving thin gold films carrying high current, electromigration may replace diffusion as the dominant method of mass

transfer[38]. Under the action of high density electric currents (10^5 amps/cm^2) a transport of metal in the direction of electron flow has been observed. This movement of gold atoms, in conjunction with the high temperatures developed, may accelerate the formation of intermetallic compounds.

3. THE DISSOLUTION OF GOLD IN MOLTEN LEAD-TIN SOLDER

3.1 Introduction

Bader[7] studied the dissolution of various metals, including gold, in molten solder by immersing a wire in a solder bath for a given time and then examining the wire microscopically to determine the decrease in diameter. A plot of decrease in diameter versus time yielded a straight line, the slope of which was the dissolution rate. Lee[19] found that the dissolution rate of a gold/15% nickel alloy was extremely low.

It was decided to study the dissolution of gold by a method different from that of Bader, in order to confirm the fact that the dissolution rate was constant with time. This was thought unlikely since gold forms intermetallic compounds with tin which are solid at the temperatures studied (200 to 315^{o}C). This incongruent dissolution will give rise to a solid reaction product layer at the gold/solder interface and it was suspected that this would cause the dissolution rate to decrease exponentially. Bader's results suggest that the compound layer has no effect upon the dissolution rate, since for the case where no solid reaction product is formed[39];

$$\text{Dissolution rate} = \frac{-dW}{dt} = kAC$$

where W = weight

A = area

C = concentration of solvent.

$$A = 2\pi r l$$

$$W = \pi r^2 l \rho$$

$$\text{Therefore } r = \left(\frac{W}{\pi l \rho}\right)^{\frac{1}{2}}$$

$$\text{and } A = 2\pi l \left(\frac{W}{\pi l \rho}\right)^{\frac{1}{2}}$$

$$= 2\left(\frac{\pi l}{\rho}\right)^{\frac{1}{2}} W^{\frac{1}{2}}$$

Therefore $-\frac{dW}{dt} = 2k \frac{\pi l}{\rho}^{\frac{1}{2}} W^{\frac{1}{2}} C$.

$$= k' W^{\frac{1}{2}}$$

$$-\int_{Wo}^{W} \frac{dW}{W^{\frac{1}{2}}} = k' \int_{o}^{t} dt$$

i.e. $2 (Wo^{\frac{1}{2}} - W^{\frac{1}{2}}) = k' t$

Therefore a plot of $(Wo^{\frac{1}{2}} - W^{\frac{1}{2}})$ against t or simply $W^{\frac{1}{2}}$ against t should give a straight line. However, W is proportional to r^2, and therefore a plot of r against t should yield a straight line, which was the case in Bader's investigation.

In this investigation a flat gold plate was used instead of a wire, and the dissolution rate was obtained by measuring weight loss rather than decrease in thickness.

For a flat plate, neglecting edge effects, the surface area A will be constant, and therefore:

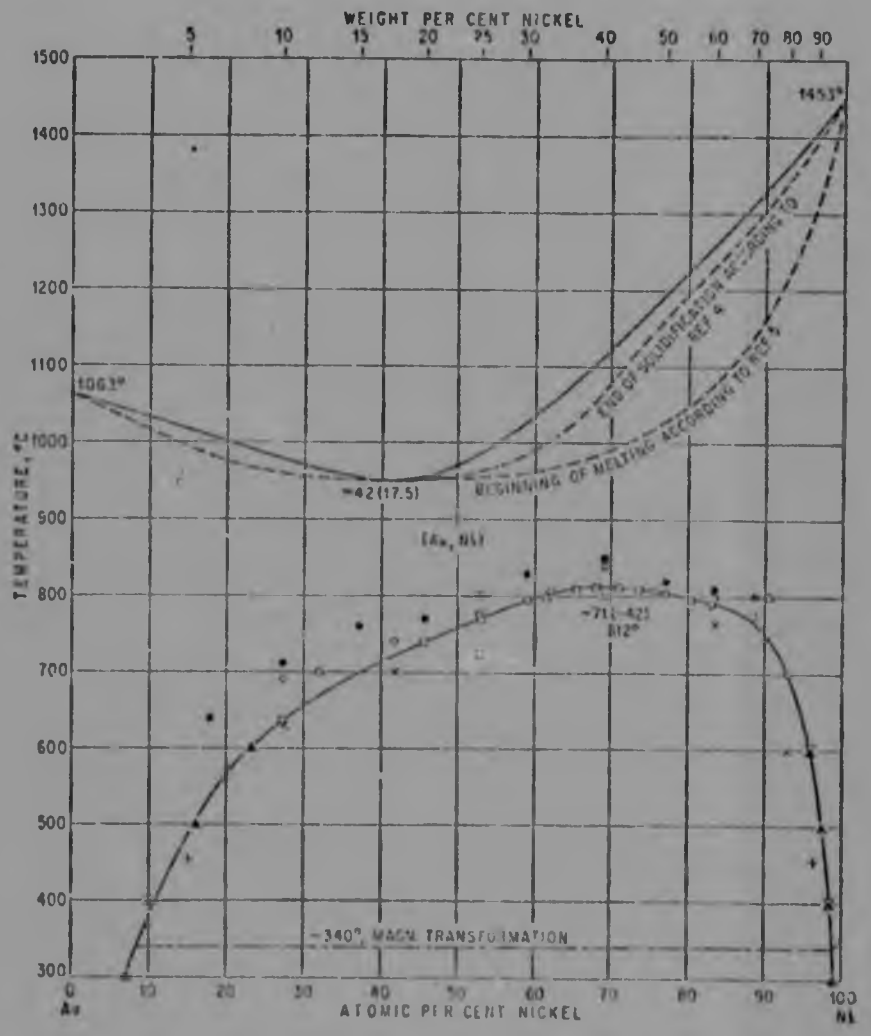
$$-\int_{Wo}^{W} dW = kAC \int_{o}^{t} dt$$

$$\therefore \quad Wo - W = k'' t$$

Hence a plot of weight loss versus time should give a straight line, if there is no diffusion barrier created to slow down the reaction.

The addition of nickel to gold is claimed by Lee[19] to reduce the dissolution in molten solder to a very low level. Lee used an electrodeposited Au - 15% Ni alloy in his investigation. It was decided to study the dissolution of alloys manufactured by melting the constituents together rather than by electrodeposition. Rapson[40] states that electrodeposited Au - Ni alloys are solid solutions, though an unstable phase may be present at low gold contents (23 to 26 atomic per cent). The Au - Ni phase diagram[22], shown in Figure 10, reveals that thermally - prepared Au - Ni alloys freeze into solid solutions in all proportions, but that a miscibility gap exists at lower temperatures. The nucleation

FIGURE 10 The Au - Ni Equilibrium Diagram



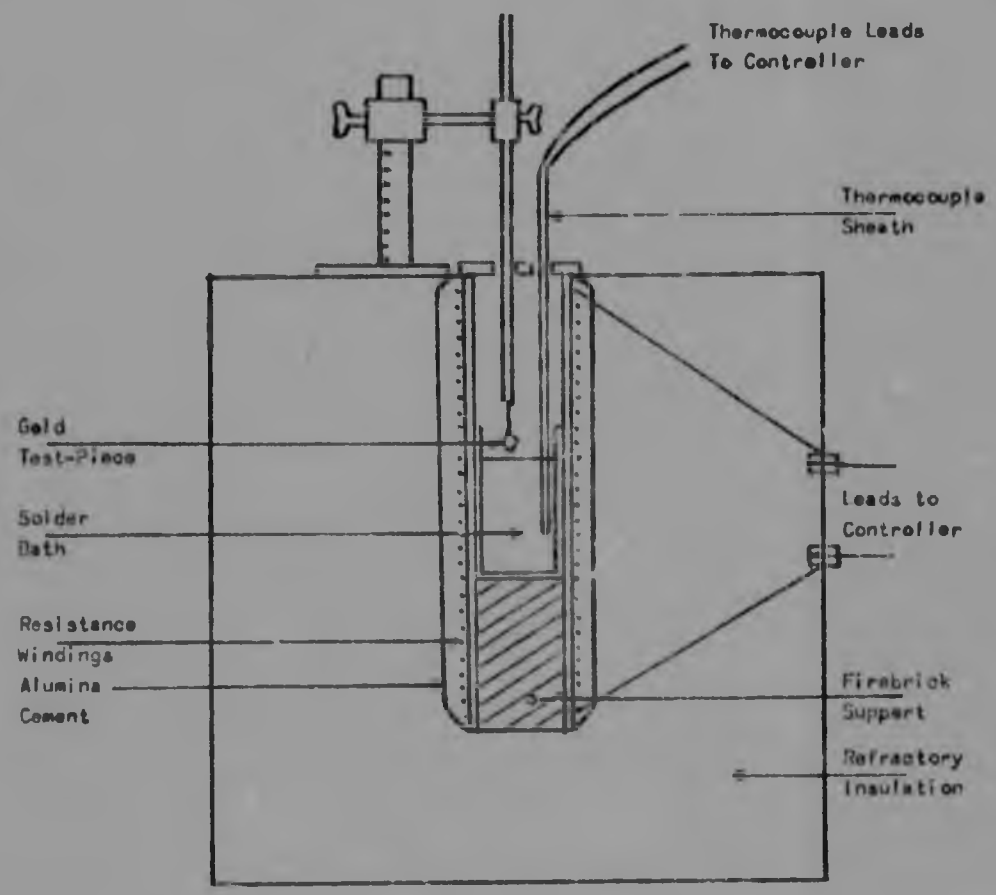
of the segregated Au - rich and Ni - rich phases is difficult and a solid solution is retained to room temperature by fast cooling through the miscibility gap[41]. The spinodal decomposition of electroplated Au - Ni solid solutions to form Au - and Ni - rich phases may be achieved by heat-treatment[40], with a resultant decrease in corrosion resistance.

3.2 Experimental Procedure

The dissolution of gold in molten lead-tin solder was studied by immersing a small, weighed gold sample in a bath of molten solder at a known temperature for a given time. The sample was then removed, quenched in water and the adhering solder was dissolved away chemically. The sample was then re-weighed and the percentage weight loss and weight loss per unit area were calculated. Fine gold (99,99% by weight) and chemically pure grade tin and lead were used throughout. Only solder of the eutectic composition was used, this being made up by melting tin and lead together in the correct proportions (63 wt.% tin) under a covering of active resin flux to prevent drossing. Samples of the solder were taken and examined under the microscope to ensure that the correct eutectic structure had been obtained, with no primary tin or lead present. A solder bath of 0,3 kilogrammes was used and this was renewed when the gold content eached 1%.

The furnace used for heating the solder, and the apparatus constructed for lowering the gold test piece into the bath are shown diagramatically in Figure (11). The furnace was heated by passing an electric current through a nichrome resistance element wound onto an alumina tube, the temperature being measured with a chromel/alumel thermocouple. The temperature in the solder bath was at first regulated by means of a variable transformer and an indicating controller, using a mechanical switching device, but this was later replaced by a solid-state electronic controller.

FIGURE 11 The Apparatus Used For Measuring the Solubility of Gold in Molten Solder



In the first set of runs performed, spherical gold test pieces weighing approximately 1 gram were used. The gold was melted on a graphite block with an oxy-acetylene flame, and due to the inability of gold to wet carbon, a spherical bead was obtained. A very fine hole was drilled through the centre of the bead in order to suspend it from a thin copper-beryllium alloy wire. The bead was then annealed at 800°C for one hour.

The solder bath was heated to the desired temperature (either 200, 220 or 240°C) and the bead was coated with resin flux prior to immersion. It was at first thought that no flux would be needed, due to the inherent nobility of gold, but it was in fact found necessary to flux the gold in order to obtain uniform wetting and reproducible results. The fluxed gold bead was then lowered to a point just above the surface of the solder bath, in order to preheat the bead and allow efficient fluxing to take place. A small quantity of flux was also added to the bath just before immersion of the bead, in order to ensure a clean, dross-free surface.

The bead was then submerged in the solder for 10 seconds, removed and rapidly quenched into water. Before the bead could be weighed to determine the weight loss, the solidified solder adhering to it had to be removed, by boiling in concentrated nitric acid which dissolved the solder and gold/tin intermetallic compounds but did not attack the gold. The bead was then re-weighed, fluxed again and re-immersed for 20 seconds. The procedure was repeated, increasing the immersion time by 10 seconds each time up to a maximum of 100 seconds. Since the gold bead was continually decreasing in size, allowance was made for this by calculating the surface area of the bead each time, and converting the weight loss to weight loss per unit area.

The results obtained from this preliminary study were highly unrel-

iable and many determinations were repeated, often with no improvement in precision. It was also an extremely lengthy procedure, due mainly to the fact that the method of dissolving away the adherent solder with nitric acid was very time-consuming. The solder was found to react rapidly at first but soon an insoluble layer of lead nitrate built up on the surface and the reaction slowed down drastically. The lead nitrate had to be removed periodically by brushing the bead with a soft wire brush.

The procedure was therefore modified as follows:

1. Instead of the repeated use of the same specimen, separate specimens of the same size and weight were used for each immersion. The new specimens were made by rolling down fine gold sheet to a thickness of 0,5 mm. and punching 5mm. square specimens out of this plate. A special punch was made for the purpose, having an internal section 5 mm. square and knife edges to provide a clean cut. The punch was made of high carbon steel and quenched and tempered to provide a durable edge. After the blanks had been punched out and a small hole made in one corner, they were annealed at $800^{o}C$ for one hour to remove work-hardening and residual stresses. This speeded up the process considerably, but consumed more gold.
2. All of the specimens were immersed in boiling resin flux, cleaned of residue by light brushing in xylol, and then stored under alcohol prior to the dissolution tests.
3. The dissolution of adherent solder in boiling nitric acid was replaced by a method using concentrated sulphuric acid and potassium hydrogen sulphate ($KHSO_4$). The specimens were placed in a saturated solution of $KHSO_4$ in concentrated sulphuric acid, heated gently to decompose the solder and then heated vigorously to expel sulphur as hydrogen sulphide. A spongy mass of lead sulphate remained and this

was removed by the addition of hydrochloric acid. This method was very much more rapid than the previous one, and when the accuracy was checked by first treating ten specimens by this method and then boiling them for three hours in concentrated nitric acid, a maximum change in weight of 0,006 grams (0,3%) was observed.

These changes improved the results considerably but the precision was still poor. It was apparent that the dissolution rate was extremely sensitive to temperature variations and it was therefore decided to improve the control of the furnace temperature. The controller first used suffered from the disadvantage that the heating current was either fully on or completely off. This gave rise to a sinusoidal variation in temperature which was aggravated by the time lag between heating of the element and heating of the solder bath, due to the low thermal conductivity of the alumina tube and crucible. The temperature variation was as much as 2°C above and below the temperature set on the controller, and this was obviously excessive for such a temperature dependent reaction.

The problem was overcome by the use of a solid-state controller of the fast-cycle, thyristor output type, and by modification of the furnace. The new controller supplied a pulsed current to the furnace windings, and as the set temperature was approached the pulse rate decreased until the system stabilised at the set point. The furnace modifications included increasing the resistance of the windings to slow down the heating rate and using a very thin-walled alumina tube to decrease temperature differences between the element and the solder bath. A second thermocouple connected to a potentiometer was introduced as a check on the temperature in the solder bath. The welded junctions of both thermocouples were immersed directly into the solder in order to minimise the time taken to respond to changes of bath temperature. The

junctions were protected from attack by the molten solder by allowing them to oxidise slightly during welding.

After these modifications had been completed, the furnace temperature was checked and found to be extremely stable. The maximum temperature variation recorded on the reference potentiometer was $\pm$ 0,01 mV. ($\pm$ 0,25^{o}C) at 200^{o}C.

In order to check the precision of the improved experimental procedure, 5 samples were immersed for 60 seconds each in a solder bath at 220^{o}C. The adherent solder was dissolved away and the samples were reweighed. The mean weight loss per unit area was 1,07 x 10^{-3} grams/mm^{2} and the standard deviation was 3,5 x 10^{-5} grams/mm^{2} or approximately 3%.

The experimental procedure was now judged to be satisfactory, and it was decided to reject all the results of the previous runs. Three new runs were performed, at 200, 220 and 240^{o}C. These temperatures were selected to lie in the range between the solidification of the solder at 183^{o}C and the catastrophic dissolution reported by Bader above 252^{o}C. This was attributed to the peritectic decomposition of $AuSn_4$ above 252^{o}C, according to the Au - Sn phase diagram (see Figure 2). Workers studying the Au - Pb - Sn ternary diagram, however, have found this reaction to occur in the range 205 to 208^{o}C[28, 29]. The experimental work showed 240^{o}C to be the practical maximum temperature anyway, since the gold test-pieces had almost completely dissolved after immersion for 100 seconds at this temperature.

The investigation was further extended to study the effect of alloying the gold with nickel. The procedure remained as before, except that the test-pieces consisted of an Au - Ni alloy instead of the pure gold used previously.

An alloy containing 5 weight per cent nickel was made up by melting the required weights of fine gold and nickel together in an alumina

crucible in a resistance heated vacuum furnace, which had been flushed with argon to remove any oxygen. Melting was performed at 1150°C after which the furnace was cooled slowly to 900°C to prevent segregation during solidification. The furnace was then cooled to room temperature in approximately five minutes by flushing with argon. The alloy bead was polished and examined under the microscope after etching with aqua regia, in order to ensure that a single-phase solid solution had been achieved. The bead was then rolled down to produce a 0,5 mm. thick sheet. During the rolling the alloy work-hardened to such an extent that it had to be annealed at 800°C for one hour to enable the necessary reduction to be achieved. The final sheet was also annealed at 800°C to remove work-hardening effects. It was noticed that a green surface discolouration was produced during annealing and this was thought to be nickel oxide. The staining was removed by treatment with concentrated nitric acid. After rolling and annealing the sheet had lost 0,04 grams from its original weight of 11,609 grams, and if this is assumed to have been nickel, the final composition was 4,67% nickel by weight.

Five mm. square test-pieces were punched out of this plate, and a dissolution test was performed at 240°C. The highest temperature was chosen in order to maximise any differences in behaviour between the alloy and the pure gold. It had also been hoped to study alloys containing 10 and 15 weight per cent nickel, but these proved to be so hard and brittle that they could not be rolled and cut into test-pieces. An Au - 15% Ni alloy was prepared, which proved to be silver in colour and so brittle that it developed radial cracks on the first passage through the rolls. It also could not be annealed completely because of severe loss of nickel by oxidation. For these reasons, the study had to be limited to an Au - 5% Ni alloy.

3.3 Results and Discussion

The results of the dissolution tests for both pure gold and the Au - Ni alloy are shown in Figure (12). The plots of wt. loss/area against immersion time yield a straight line in every case, confirming the results of Bader. The line for the Au - 5% Ni alloy shows an initial rapid dissolution rate, similar to that of pure gold, followed by a much lower rate. This was probably due to the loss of nickel from the surface layer of the sheet during annealing.

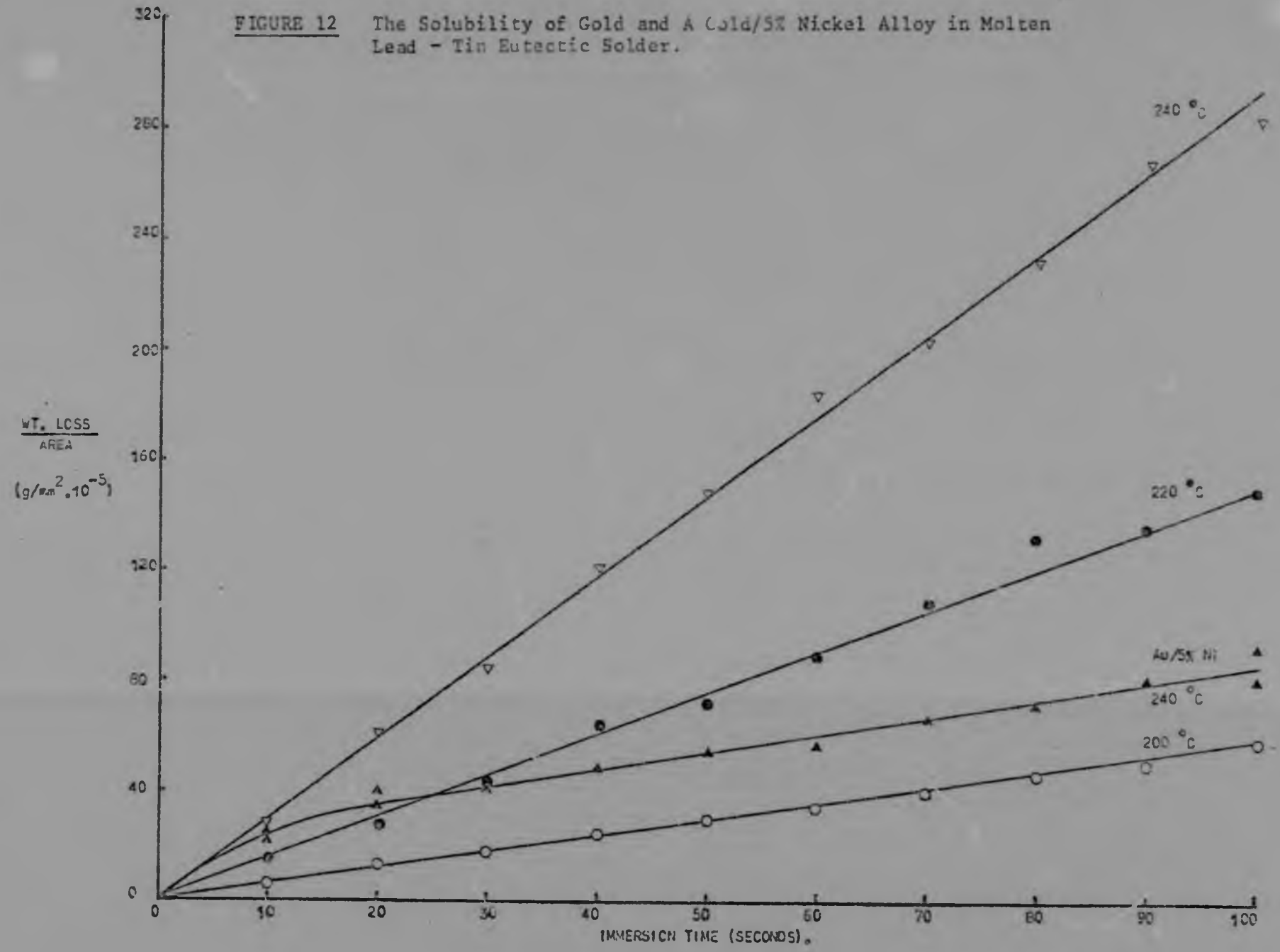
The most obvious fact which can be seen from Figure (12) is that the influence of temperature upon the dissolution rate is profound. A rise in temperature of 20°C approximately doubles the dissolution rate. The dissolution rate is given by slope of the line in each case, as below:

Temperature (°C)	Dissolution Rate ($gm/mm^2/sec. \times 10^{-5}$)
200	0,56
220	1,48
240	2,93
Au - 5% Ni 240	0,88

The maximum dissolution rate was recorded at 240°C. If the units are converted to microns/second, this corresponds to a dissolution rate of 1,7 microns/second on each side of the test-piece. Bader's experiments using a gold wire, yielded radial dissolution rates of 3 and 4 microns/second at 232 and 252°C respectively. However, as pointed out in the introduction to this chapter, the linear dissolution rate for a plate should be the square root of that for a wire, since the area of a plate remains constant while that of a wire decreases by a term involving $(radius)^2$. Thus the agreement with the results of Bader is fairly close.

The addition of as little as 5% of nickel to the gold decreases its solubility markedly. The reason for this is not clear, for while nickel is insoluble in solder, a lattice of gold atoms containing nickel in these low proportions should be soluble. No nickel-rich phase could be

FIGURE 12 The Solubility of Gold and A Gold/5% Nickel Alloy in Molten Lead - Tin Eutectic Solder.



distinguished under the microscope and any nickel oxide which may have formed on the surface should have been dissolved in the concentrated nitric acid with which the plate was treated after annealing. If a nickel oxide film had been present, the solder would have had difficulty in wetting the surface, but this was not found to be a problem.

Nickel is not readily wetted by solder, however, and the addition of small amounts of nickel to gold may reduce the wettability, thereby decreasing the dissolution rate.

3.4 Conclusion

The dissolution of gold in molten solder is very rapid and highly temperature-dependent. The dissolution rate is not decreased by the formation of solid gold/tin intermetallic compounds at the interface. The only explanation for this is that these compounds must dissolve into the solder as rapidly as they are formed, thus preventing the build-up of a massive interfacial compound layer.

A gold - 5% nickel alloy was found to dissolve at approximately one-third of the rate of pure gold. The reasons for this are not apparent, and this is a field worthy of further study. If the corrosion-resistance and solderability of gold/nickel alloy electroplate prove satisfactory, the replacement of gold plate by this material may prevent intermetallic compound formation and embrittlement of soldered joints.

At 200°C, which is the lowest practical soldering temperature, the dissolution rate was found to be $0{,}56 \times 10^{-5}$ gm./mm^2/ second, which corresponds to approximately 0,4 microns/second. Thus commercially used gold plate, which is typically 3 to 5 microns in thickness, will dissolve completely in approximately 10 seconds, even at this low temperature. The recommendation that soldering temperature and time be kept to a minimum is therefore of limited value.

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4. COMPOUND FORMATION DURING SOLDERING TO GOLD

4.1 Introduction

Intermetallic compounds, usually in the form of acicular crystals, have been observed in the great majority of joints made between gold or gold-plated surfaces using a lead-tin solder. Several investigators[1, 4, 7, 9, 18] have assumed this compound to be $AuSn_4$ and have noted its occurence both as needles in the solder and as a continuous film at the gold/solder interface. It has also been suggested that the interfacial compound layer is in fact AuSn[21]. Electron microprobe studies reported in a review by Thwaites[21] indicated that both the acicular compound and the interfacial compound were $AuSn_4$ which contained up to 19% lead.

In view of the uncertainty prevailing as to the exact nature of the compound or compounds formed, it was decided to study the metallurgical reactions which occur between gold and tin during soldering and ageing at elevated temperatures. Prince[27, 28] and Karnowsky and Rosenzweig[29] have shown that lead will not form any compounds until the gold content of the solder exceeds 50 atomic per cent.

From thermodynamic data published by Hultgren et al[23], the free energies of formation of the compounds AuSn, $AuSn_2$ and $AuSn_4$ have been calculated at various temperatures.

These are given in the table below:

Temperature		Free Energy of Formation (kilojoules/g.-atom)		
(^oK)	(^oC)	AuSn	$AuSn_2$	$AuSn_4$
298	25	-14,923	-12,623	-7,565
473	200	-14,747	-11,850	-7,348
493	220	-14,718	-11,795	-7,378
513	240	-14,688	-11,720	-7,386

Thus all three compounds are stable to room temperature, with the

stability decreasing in the order AuSn, $AuSn_2$, $AuSn_4$.

4.2 Experimental Work and Results

In a preliminary study, specimens were made up by melting lead-tin solder of the eutectic composition around small gold beads. An electrically-heated soldering iron with a temperature regulated tip was used to prepare the specimens, and the temperature of the tip was measured by means of a thermocouple and found to be in the range 340 - 380°C. A commercially available resin flux was used to ensure the production of a sound bond between the gold and the solder.

Various types of specimen were produced and the microstructures obtained are described below:

a) Small gold substrate with a large solder fillet. (High soldering temperature).

In this case, the weights of the gold bead and the solder fillet were approximately equal. The gold bead was preheated on a glass plate and the solder was then melted around it. The solder was seen to wet the gold and then a sudden, rapid reaction was observed and a solid, granular reaction product which completely surrounded the gold was formed. The joint was sectioned and observed under the microscope, where the gold was found to have been catastrophically attacked by the solder, (See Plate 1) leading to the production of an intermetallic compound which was solid at the soldering temperature, and was therefore identified as AuSn. This bears out the findings of Bader[7] that at high temperatures gold dissolves very rapidly due to the instability of $AuSn_4$.

b) Large gold substrate with a small solder fillet. (Low soldering temperature).

In this case, the gold was not preheated and a small amount of solder was used in an attempt to keep the temperature low enough to prevent

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b) Large gold substrate with a small solder fillet. (Low soldering temperature).

In this case, the gold was not preheated and a small amount of solder was used in an attempt to keep the temperature low enough to prevent

Plate 1 (X 33)

Gold soldered at high temperature. The gold has been severely attacked, with resultant massive formation of AuSn. Unetched.

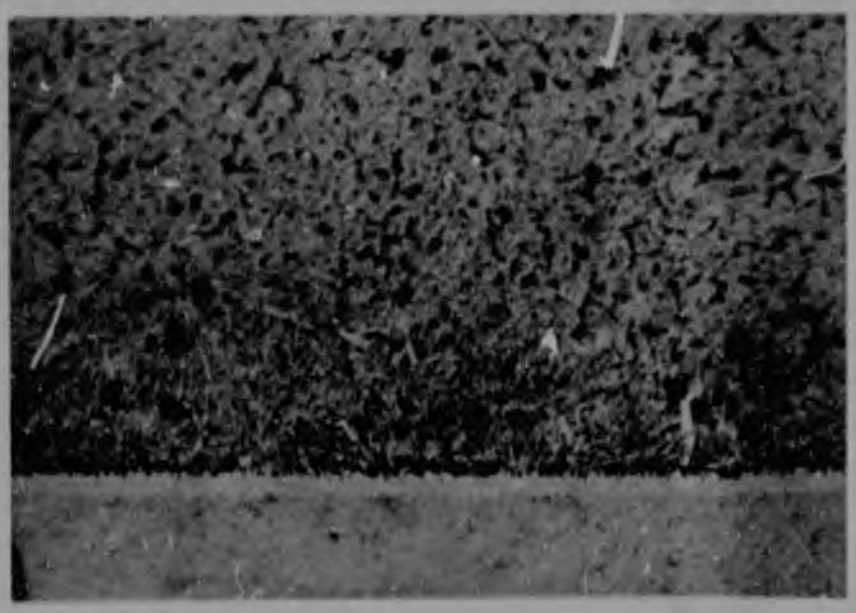

Plate 2 (X 400)

Gold/solder interface of a fluxed specimen. Note the continuous compound layer at the interface and the acicular compound in the solder adjacent to it. Etched with HNO_3/CH_3COOH in glycerine.

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catastrophic dissolution. Two specimens were prepared, one with and one without flux. In the unfluxed case, a contact angle of approximately 45° between the gold and the solder was obtained, while in the fluxed case, this angle was approximately 10°.

When the joints were sectioned and examined microscopically, a thin white layer of intermetallic compound was observed at the interface between the gold and the solder, as well as acicular crystals in the solder adjacent to the compound layer. In the fluxed specimen this layer was continuous (Plate 2) while in the unfluxed specimen there were areas where no compound had formed, due to bad wetting of the gold. The interfacial compound layer was too thin to be identified under the microscope, and the attempts made to identify this layer will be described in the following section of this chapter.

The above two specimens were then aged at 100°C for 120 days, in order to determine whether the interfacial compound layer increased in thickness. The specimens were immersed in an oil bath which was kept in an oven regulated at 100°C. When the specimens were re-examined after the ageing treatment, the compound layer was seen to have increased greatly in thickness, and was also now seen to consist of two compounds with a sharply defined junction between them (See Plates 3 and 4). The specimens were not etched, but a difference in hardness gave rise to a relief effect on polishing, which served to delineate the boundary between the two compounds. In the case of the fluxed joint, the total thickness of the compound layer had increased from 6 to 60 microns during the ageing treatment. The structure of the lead-tin eutectic solder was also seen to have coarsened considerably during the ageing treatment. A high proportion of free lead was present immediately adjacent to the compound layer, due to the consumption of tin by reaction with gold during ageing.

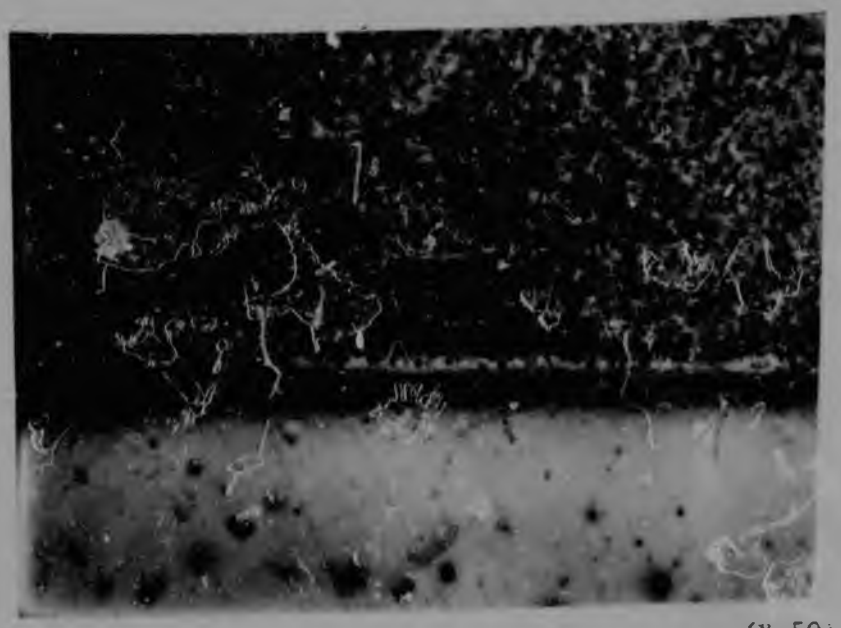


Plate 3 (X 50)

Fluxed specimen after ageing at 100°C for 120 days. There has been definite growth of the compound layer which can now be resolved into two distinct compounds. Unetched - compounds distinguished by relief effect after long polishing.

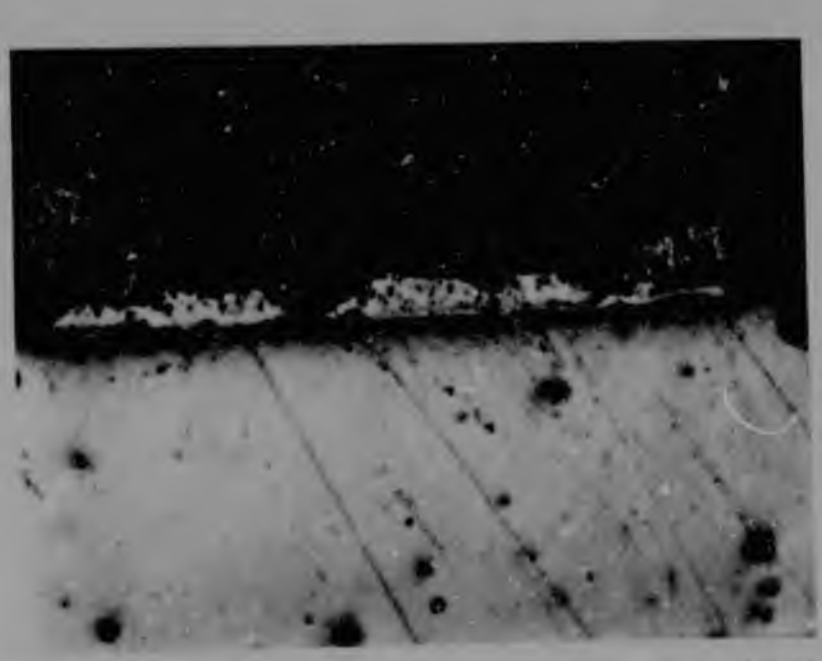


Plate 4 (X 50)

Unfluxed Specimen after ageing at 100°C for 120 days. Again there has been considerable growth of the duplex compound layer. Unetched.

In order to determine whether two compounds were formed on soldering, or whether the second compound only appeared during ageing, a small, fluxed gold sphere was held in a small volume of solder at 200°C for 300 seconds, after which the solder was allowed to solidify. The specimen was then sectioned and examined. This method produced an interfacial compound layer of 10 to 15 microns in thickness, enabling microscopic examination at reasonable magnification. The specimen was etched in a solution of 15% nitric acid and 15% acetic acid in glycerine before examination.

This specimen revealed two compounds at the interface, in the form of a thin continuous layer adjacent to the solder (Plates 5 and 6). Material which appeared to have broken away from the outer compound layer was also present to a considerable distance into the bulk of the solder, while free lead was once again observed adjacent to the compound layer.

4.2.1 The Identification of Compounds Formed During Soldering and Ageing

X-ray powder diffraction methods were used in an attempt to identify the compounds formed at the gold/solder interface during soldering and ageing. The powder diffraction index was found to contain d-spacing data for gold, tin, lead and the compound AuSn, but not for the compounds $AuSn_2$ and $AuSn_4$. It was therefore necessary to determine the d-spacings for these compounds and this entailed their preparation from the pure constituent metals.

The three compounds AuSn, $AuSn_2$ and $AuSn_4$ were prepared by melting the correct weights of gold and tin together in graphite crucibles under a covering of carbon to prevent loss of tin by oxidation. The temperatures at which the alloys were manufactured and annealed were selected from the Au-Sn phase diagram (Figure (2)) as in the table below:

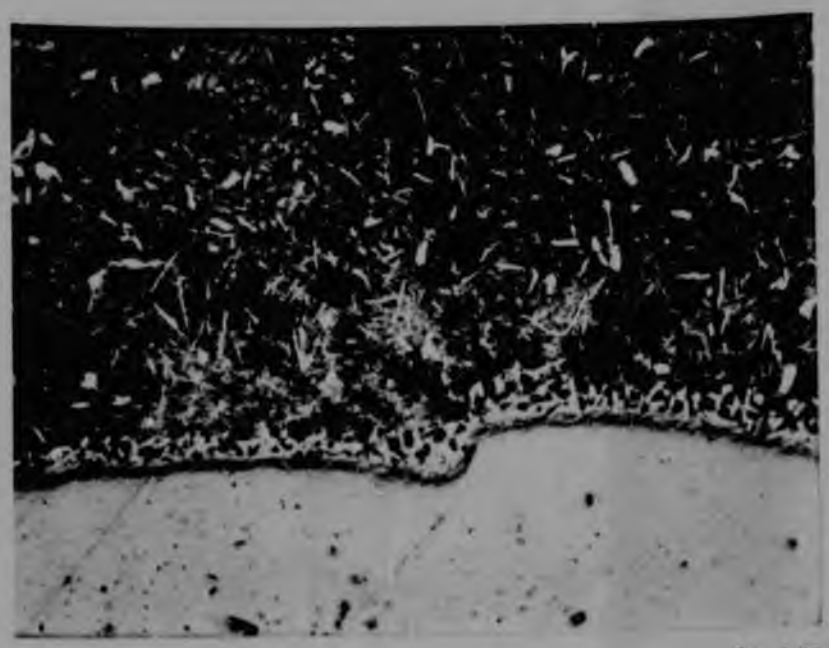


Plate 5 (X 100)

Gold and solder reacted at 200°C for five mintues. Note the compound layer at the interface and the acicular compound in the bulk of the solder. Etched with HNO_3/CH_3COOH in glycerine.

Plate 6 (X 350)

Plate 5 at higher magnification. Note the duplex compound layer and the free lead adjacent to it. Etched with HNO_3/CH_3COOH in glycerire.

Compound	Melting Point or Decomposition Temperature (^{o}C)	Manufacturing Temperature (^{o}C)	Annealing Temperature (^{o}C)
AuSn	418	450	250
$AuSn_2$	309	400	200
$AuSn_4$	252	400	200

In each case, the graphite crucible was introduced into a vertical tube furnace at the required temperature, held for 30 minutes and then cooled to the annealing temperature. After annealing for 20 hours the crucible was cooled to room temperature in the furnace. In none of the cases was there a difference of greater than one per cent between the initial and final weights of the alloy.

The resultant alloy beads were crushed to a fine powder in an agate mortar under alcohol. All three of the compounds were extremely brittle and crushed easily. A small amount of each compound was then mixed with rubber cement and mounted in a Debye-Scherrer powder diffraction camera.

An X-ray diffraction pattern was obtained for each compound, using Cu Kα radiation with a nickel filter and a exposure time of six hours. The relative intensities of the lines obtained on the film were estimated visually, and d-spacings for the three compounds were calculated. The d-spacing obtained experimentally for the compound AuSn were in good agreement with those given in the powder diffraction file. The data determined for three compounds are given in Figure (13).

Having obtained the diffraction patterns for the three compounds, and knowing the d-spacings for gold, lead and tin, it was hoped to identify the unknown compounds by comparison of their diffraction patterns with these. Accordingly, samples of the interfacial compound observed under the microscope were removed with a sharp needle and mounted in the diffraction camera. Patterns were obtained and compared

COMPOUND : AuSn.

d = 2,22	2,16	3,74	3,74
I/I_1 = 100	65	50	50

Colour: BRIGHT SILVER
METALLIC LUSTRE.

d (A)	I/I_1
3,74	50
3,09	45
2,22	100
2,161	65
1,870	8
1,772	10
1,702	4
1,652	10
1,549	25
1,415	10
1,370	8
1,259	20

COMPOUND : $AuSn_2$.

d = 2,06	2,03	2,74	4,45
I/I_1 = 100	70	70	20

Colour: SILVER GREY
METALLIC LUSTRE.

d (A)	I/I_1
4,45	20
3,72	10
3,40	10
3,06	40
2,91	60
2,74	70
2,39	30
2,11	40
2,06	100
2,03	70
1,90	60

COMPOUND : $AuSn_4$.

d = 2,16	2,02	2,96	5,74
I/I_1 = 100	100	80	40

Colour: SILVER GREY
METALLIC LUSTRE.

d (A)	I/I_1
5,74	40
4,26	30
2,96	80
2,83	60
2,29	30
2,17	100
2,08	40
2,02	100
1,46	50
1,42	50
1,30	30

Figure 13 D-Spacing Data Obtained for the Compounds AuSn, $AuSn_2$ and $AuSn_4$.

with the standards previously derived. After several unsuccessful attempts in which the only lines observed corresponded to lead and tin, a pattern was obtained with several faint lines corresponding to the compound $AuSn_4$. Longer exposure improved the definition and more lines became visible. Some of these, however, were found to correspond with the lines for $AuSn_2$ and AuSn and the problem was further complicated by the close proximity of some of the lines for gold, tin and lead to those obtained for the compounds. A typical analysis of the diffraction pattern obtained from a specimen aged at 100°C for 120 days is shown in Figure (14). The results are somewhat inconclusive, with evidence of the presence of all three compounds, with $AuSn_4$ predominating. In an attempt to obtain a thicker compound layer at the interface, a specimen was aged at 200°C. Once again evidence of all three compounds was found, but in this case AuSn appeared to predominate.

It was obvious that the X-ray method was not sufficiently precise, and it was therefore decided to approach the National Institute for Metallurgy (N.I.M) for the use of their electron microprobe analyser. Permission was kindly granted and two specimens were submitted for analysis. Since the compound layer obtained after soldering was too thin for accurate analysis, two samples which had been aged at 100°C for four months were selected (Plate 3 and 4). These were analysed by N.I.M. on an ARL-FMX electron microprobe, using an accelerating voltage of 25kV and a beam current of 0,04 micro-amps. Standards used were the compound AuSn prepared previously, and analysed galena for the determination of lead. Both samples and standards were coated with carbon before analysis, and the data obtained were processed by a computer to yield final analyses in terms of weight percentages.

In the case of the fluxed specimen (Plate 3), the compound adjacent to the gold surface was found to have the formula $Au_1Sn_{1,899}Pb_{0,02}$ while

SAMPLE AGED AT 100° C FOR 120 DAYS. IRRADIATED FOR 7 HOURS WITH $Cu\ K_{\alpha}$ RADIATION.

d-SPACING.	PROBABLE SOURCE.	POSSIBLE SOURCE.
4,26	$AuSn_4$ (4,26)	
3,74	AuSn (3,74)	$AuSn_2$ (3,72)
2,97	$AuSn_4$ (2,96)	Sn (2,92), $AuSn_2$ (2,91)
2,84	Pb (2,86), $AuSn_4$ (2,83)	
2,62		
2,47	Pb (2,48)	
2,35	Au (2,355)	$AuSn_2$ (2,39), $AuSn_4$ (2,29)
2,25	AuSn (2,22)	$AuSn_4$ (2,29)
2,17	$AuSn_4$ (2,17)	AuSn (2,16)
2,08	$AuSn_4$ (2,08)	$AuSn_2$ (2,11), Sn (2,06)
2,03	$AuSn_2$ (2,03)	Au (2,04), $AuSn_4$, Sn (2,02)
1,74	Pb (1,75)	
1,60		Sn (1,66), AuSn (1,55)
1,49	Pb (1,49), Sn (1,48)	$AuSn_4$ (1,46)
1,44	Sn, Au (1,44)	Pb (1,43), $AuSn_4$ (1,46)
1,42	$AuSn_4$ (1,42)	Pb (1,43)
1,30	$AuSn_4$, Sn (1,30)	
1,23	Au (1,23)	Sn (1,21)
1,18	Au (1,18)	AuSn (1,16)

COMMENT. NO DIRECT CONCLUSION CAN BE DRAWN FROM THESE RESULTS. ALL THOSE LINES WITH TWO OR MORE PROBABLE SOURCES MUST BE DISREGARDED, AS MUST THOSE DERIVED FROM Au, Sn OR Pb. THE REMAINING LINES INDICATE THE PRESENCE OF ALL THREE OF THE COMPOUNDS, WITH $AuSn_4$ PREDOMINATING.

Figure 14 A Typical Analysis of the Diffraction Pattern Obtained From An Unknown Interfacial Compound.

that adjacent to the solder was found to be $Au_1Sn_{3,77}Pb_{0,06}$. In the unfluxed specimen (Plate 4) the corresponding areas had the formulae $Au_1Sn_{2,01}Pb_{0,03}$ and $Au_1Sn_{3,97}Pb_{0,1}$. Thus the compounds are the same in both cases and consist essentially of $AuSn_4$ and $AuSn_2$ with a very low lead content. There was no indication of the presence of AuSn or of the incorporation of lead into the $AuSn_4$ structure, as reported by Thwaites in his review of the metallurgical reactions that occur during soldering on gold[21].

4.2.2 A Study of the Reactions Between Gold and Molten Tin

Previous studies of joints between gold and lead-tin solder, using both the optical microscope and the electron microprobe, had identified a duplex $AuSn_4/AuSn_2$ layer at the interface and acicular $AuSn_4$ crystals in the bulk of the solder. Since the lead acts only as a diluent and forms no compounds with gold in the presence of tin, it was decided to react pure gold and pure tin together at various temperatures and study the resultant microstructures. The specimens were made up by melting a small amount of tin in an alumina crucible, adding a preheated gold bead, and allowing various times for reaction to proceed. The resulting Au-Sn alloy beads were polished on the lower surface of the bead and examined microscopically and by X-ray diffraction analysis.

The microstructures were first examined in the unetched condition since the various Au-Sn compounds differ in hardness and a pronounced relief effect often indicated the structure. They were then etched in a solution of 15% HNO_3/15% CH_3COOH/70% glycerine (etchant No. 1) which produces a golden-brown coloration on $AuSn_4$ and does not affect the other compounds. A second etching operation with etchant No. 2 (50% HNO_3/50% water) was then performed. Etchant No. 2 produces severe pitting on tin, turns $AuSn_4$ a dark brown colour, gives a straw-yellow to gold coloration on $AuSn_2$ and has no effect on AuSn. AuSn could often be distinguished

by its pinkish colour under low illumination, even in the unetched condition.

Thus by progressive etching the constituent compounds could be identified. Confirmation of these findings was provided by X-ray diffraction analysis. The polished specimen was placed in the goniometer in place of the normal powder sample and a diffraction pattern of the surface was obtained. This method did not indicate which phase was which, but merely indicated which compounds were present in the area being irradiated. The intensities of the peaks for the various compounds also provided a rough indication of the relative amounts in which they were present. This method is not sensitive enough to identify phases in small concentrations, but used in conjunction with the microscopic techniques it enabled the microstructures to be analysed. These are summarised below:

(a) Specimen 1 (See Plates 7 and 8)

In this specimen gold and tin were reacted together at 245°C for five minutes, and then cooled in air. Reference to the gold-tin equilibrium diagram (Figure 2) will indicate that $AuSn_4$ is the stable phase at this temperature. It was noted that the alloy remained liquid at all stages during the reaction and this indicates that less than 10% of gold could have been present in the tin otherwise the alloy would have solidified. Thus the structure could be expected to consist of primary $AuSn_4$ and the $AuSn_4$-Sn eutectic. This was in fact the case, with acicular needles of $AuSn_4$ radiating outwards from the gold bead, in an $AuSn_4$-Sn eutectic matrix. There was a duplex compound layer at the interface, consisting of $AuSn_2$ adjacent to the gold and $AuSn_4$ adjacent to the tin. The $AuSn_2$ must have formed initially as a solid layer at this temperature and then reacted with the molten tin to form $AuSn_4$. Thus the formation of compounds at the interface is controlled by the concentration gradient of gold in the liquid tin. The dissolution reaction can be visualised as the reaction

Plate 7 (X 70)

Specimen 1. Needles of $AuSn_4$ radiating outwards from the surface of the gold bead. The matrix consists of the $AuSn_4$-Sn eutectic. Etched with HNO_3/CH_3COOH in glycerine.

Plate 8 (X 500)

Specimen 1 at high magnification. The duplex interfacial compound layer consists of $AuSn_2$ adjacent to the gold and $AuSn_4$ adjacent to the tin. Needles of $AuSn_4$ radiate outwards from the compound layer. Etched with 50% HNO_3.

of Au and Sn to form solid $AuSn_2$ at the interface, which then reacts with more tin to produce $AuSn_4$, also solid at this temperature. Gold is dissolving continuously into the tin from this $AuSn_4$ layer, and on cooling this precipitates out as primary crystals of $AuSn_4$, followed by the $AuSn_4$-Sn eutectic at 217°C, at which temperature the alloy is finally solid. This mechanism complies with previous findings that the dissolution rate does not decrease with time i.e., the solid layer at the interface does not impede dissolution, only if the rates of the reaction (1) and (2) below are sufficiently high to prevent the build-up of a massive interfacial compound layer.

(1) $AuSn_{2(s)} + Sn_{(l)} \longrightarrow AuSn_{4(s)}$

(2) $AuSn_{4(s)} + Sn_{(l)} \longrightarrow (Au)_{Sn}$

(b) Specimen 2 (See Plate 9)

In this case, gold and tin were reacted at 275°C for one minute, i.e. the compounds $AuSn_2$ and $AuSn_4$ should have been formed. Once again the alloy remained liquid throughout the reaction, therefore it could not have contained more than 15 - 20% gold in solution. Microscopic examination of the specimen revealed a very thin duplex $AuSn_4/AuSn_2$ layer around the gold bead and needles of $AuSn_4$ radiating outwards from the bead. There were also several needles of primary $AuSn_2$, which were surrounded by $AuSn_4$ as a result of the peritectic decomposition of $AuSn_2$ on cooling below 252°C. Some of the $AuSn_4$ in areas away from the gold bead was present as large, blocky particles. The $AuSn_4$-Sn eutectic mixture provided the matrix between the compound needles.

X-ray analysis of the specimen gave definite evidence of the presence of $AuSn_4$, Au and beta-tin, as well as a tentative indication of the presence of $AuSn_2$. This confirmed the microscopic interpretation since the $AuSn_2$ was only present in very small amounts widely dispersed

Plate 9 (X 79)

Specimen 2. The thin duplex needles are $AuSn_2$ surrounded by $AuSn_4$. The thicker grey needles are primary $AuSn_4$ and the black matrix is the $AuSn_4$-Sn eutectic. Etched with HNO_3/CH_3COOH in glycerine.

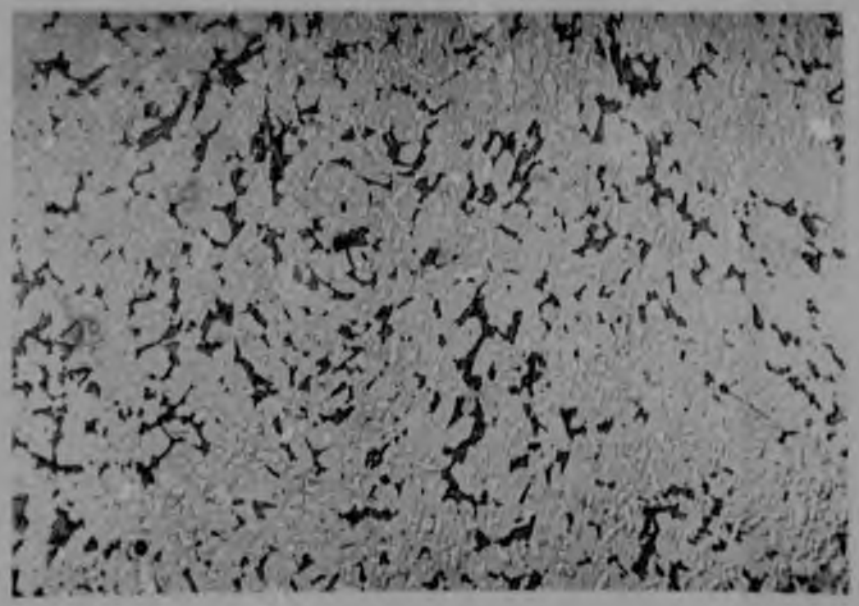


Plate 10 (X 70)

Specimen 3. Duplex dendrites with AuSn in the centre, surrounded by $AuSn_2$ as a result of the peritectic decomposition reaction at $309^{\circ}C$. The dark phase is $AuSn_4$. Etched with 50% HNO_3.

throughout the matrix.

(c) Specimen 3 (See Plate 10)

This specimen was prepared by reacting gold and tin at 275°C for five minutes. The rate of dissolution at this temperature is very high and all of the gold dissolved to form various compounds. The microstructure consisted of three distinct regions which are discussed below.

One region, presumably that of highest gold concentration, consisted of dendrites of $AuSn_2$ with a central core of AuSn and a few small interdendritic areas of $AuSn_4$. The second region again contained duplex $AuSn/AuSn_2$ dendrites but the proportion of interdendritic $AuSn_4$ was much greater. The third area, a small circular region in the centre of the bead, contained no AuSn but consisted of needles of $AuSn_2$ and $AuSn_4$ in the eutectic matrix. This structure was also present on the edge of the bead furthest away from the area of highest gold concentration. X-ray analysis confirmed the presence of all three compounds mentioned above.

In this case, the reaction time was long enough to enable certain areas to attain the stoichiometric AuSn composition, even at this relatively low temperature, and the cooling rate was sufficiently high to prevent complete dissociation of the AuSn to form $AuSn_2$. The almost complete lack of eutectic mixture implies that the bottom of the alloy bead was made up of solid compounds while the top, being of lower gold content, was still liquid. The small circular area in the centre may have been a pipe or shrinkage cavity.

(d) Specimen 4 (See Plates 11 and 12)

In this instance, gold and tin were reacted at 330°C for one minute. Microscopic examination revealed two distinct regions, one of which consisted of duplex $AuSn$-$AuSn_2$ dendrites in an $AuSn_4$ matrix. The other region contained needles of $AuSn_2$ in an $AuSn_4$ matrix with small particles of AuSn at the centres of some of the needles. There were also some

Plate 11 (X 140)

Specimen 4. Duplex AuSn/$AuSn_2$ dendrites in an $AuSn_4$ matrix. Etched with 50% HNO_3.

Plate 12 (X 70)

Specimen 4. In this area, presumably of lower gold content, there is little primary AuSn. The structure consists of primary needles of $AuSn_2$ in a matrix of $AuSn_4$. Note the cracking and drag-out of the brittle $AuSn_2$. Etched with HNO_3/CH_3COOH in glycerine.

small, widely spaced areas of the $AuSn_4$-Sn eutectic and the $AuSn_2$ phase in particular exhibited considerable drag-out and cracking.

It appears that primary AuSn forms as dendrites which partially decompose on cooling to produce an outer layer of $AuSn_2$. Primary $AuSn_2$, however, forms as needles which once again partially decompose to form $AuSn_4$. Thus the dendritic area of the specimen contained a high concentration of gold, leading to the formation of primary AuSn, whereas the other area only contained sufficient gold to produce $AuSn_2$.

(e) Specimen 5 (See Plate 13)

Gold and tin were reacted together for five minutes at 330°C to produce this specimen. In the unetched condition, the microstructure revealed gross porosity which had resulted from the drag-out of an intergranular phase during polishing. Etching the specimen with etchant number 1 enabled the remaining areas of this phase to be identified as $AuSn_4$. When etched with etchant number 2, the remainder of the specimen was resolved into large duplex grains consisting of AuSn surrounded by $AuSn_2$. The structure was uniform throughout the specimen and many of the grains exhibited severe cracking, probably due to thermal contraction.

4.3 Discussion

It has been shown that unless the soldering temperature is kept below 250°C, an extremely rapid reaction between gold and molten solder occurs, with the production of a massive layer of AuSn. This is obviously detrimental to joint strength since the compound is very brittle. At lower soldering temperatures, a duplex compound layer is produced at the gold/solder interface, consisting of $AuSn_2$ and $AuSn_4$. This layer was seen to increase in thickness upon ageing at 100°C, and this growth may lead to the establishment of shear stresses at the interface. These interfacial stresses may either cause or facilitate separation. This in turn will explain why joints which are of satisfactory strength

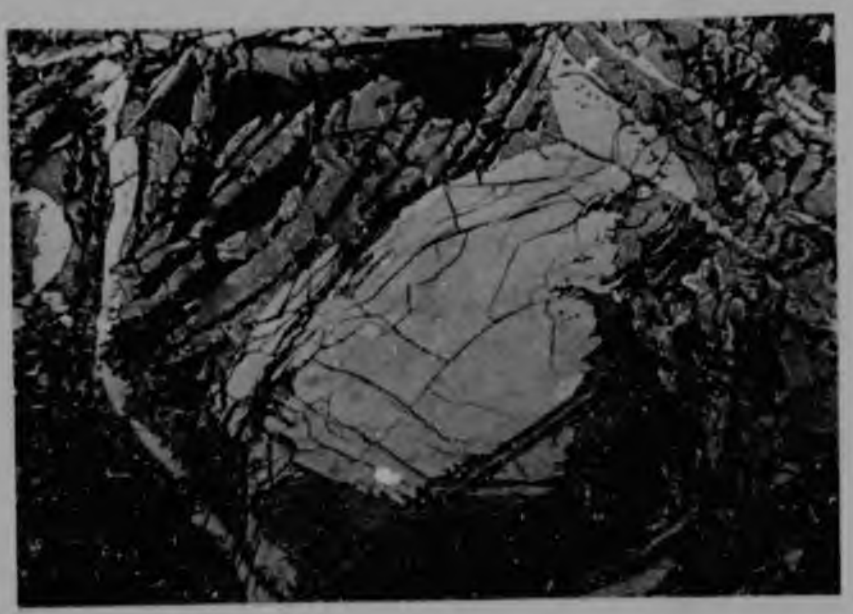


Plate 13 (X 70)

Specimen 5. The large central grain is AuSn, surrounded by $AuSn_2$. The porosity is due to the removal of $AuSn_4$ during polishing. Note the severe cracking of both AuSn and $AuSn_2$. Etched with 50% HNO_3.

in the as-soldered condition are found to have separated under little or no applied stress after operation for long periods at moderate temperatures.

The following conclusions can be drawn from the study of the reactions which take place between gold and molten tin:

a) Under non-equilibrium conditions (as is the case in a soldered joint) the type of gold/tin compound which forms is dependent upon the temperature and the concentration of gold in each particular area of the specimen.

b) The duplex $AuSn_4/AuSn_2$ interfacial layer is present even up to 275°C. The absence of AuSn from this layer is due to the fact that the concentration of gold in the tin immediately adjacent to the gold surface is equal to the solubility at that temperature. At temperatures below 300°C, the solubility is too low for AuSn to form and thus a layer of $AuSn_2$ forms adjacent to the gold surface. Above this temperature, the solubility is high enough for AuSn to form, but the dissolution is so drastic that no unreacted gold remains.

c) The peritectic decomposition reactions:

$$AuSn + Sn \longrightarrow AuSn_2 \qquad (309^{\circ}C)$$

and

$$AuSn_2 + Sn \longrightarrow AuSn_4 \qquad (252^{\circ}C)$$

are fairly sluggish and give rise to duplex compound particles. Primary AuSn is dendritic while primary $AuSn_2$ is acicular and the decomposition product forms a layer surrounding the primary compound in each case.

d) The compounds AuSn, $AuSn_2$ and $AuSn_4$ are all hard and brittle, $AuSn_2$ in particular showing cracks and drag out as a result of polishing. Both $AuSn_2$ and $AuSn_4$ form in long, thin needles and thus their presence is especially detrimental to the strength of a soldered joint. The

duplex $AuSn_2/AuSn_4$ compound layer at the Au-Sn interface is also detrimental to joint strength, especially since these compounds grow during ageing at 100°C, and differential growth rates may set up a shear stress at the interface.

5. THE TENSILE PROPERTIES OF SOLDERED JOINTS BETWEEN BOTH PURE GOLD AND GOLD-PLATED SURFACES

5.1 Introduction

To determine the effects of the fundamental phenomena studied, it was necessary to develop a method for testing the strength of soldered joints, which would yield results of practical significance. The technique was also required to be accurate and precise, and accordingly the soldering operation had to be as free of the human element as possible. Hand soldering of the joints was therefore rejected as being too difficult to control.

The joint design had to be selected in order to yield information which was applicable to the types of soldered joint encountered in practice. Direct tensile stresses are seldom encountered in industrial soldered joints, the more usual design being such as to subject a thin solder layer to a shear stress, e.g. the soldering of wires into holes on printed circuit boards. It was therefore decided to construct soldered lap joints which were to be tested in shear as opposed to direct tension.

The investigation consisted of two parts. The first tests were performed on joints made between fine gold surfaces, the variables studied being the temperature of soldering and the time of ageing at 100°C after soldering. In the second series of tests, various commercial gold electroplates were used. A single soldering temperature was selected and the variables studied were the type of gold plate, the thickness of the gold layer, the effect of a nickel undercoat and the time of ageing at 100°C after soldering.

5.2 Tests on Joints Between Pure Gold Surfaces

5.2.1 Experimental Work

Previous investigators[1, 2, 19] had all made use of gold-plated copper strip for the construction of soldered lap joints. In these cases the

copper substrate provided the necessary load-bearing capacity to ensure that fracture occurred at the soldered joint before yielding of the copper took place. In this case, however, the very low yield stress of fine gold made it impossible to construct lap joints out of gold strip, and the cost would have been prohibitive even had this been possible.

For these reasons a composite test piece was developed. The load-bearing member consisted of a 60% Cu - 40% Zn brass bar to which a small gold coupon was silver-soldered at one end. A sketch of an assembled lap joint is shown in Figure 15. The detailed construction of the joint is described below.

A 5mm square brass bar was cut into 50mm lengths and these were bent in a vice, between platens which each had a 5mm high step machined in them, the one step being offset from the other by 25mm. This produced the necessary shape to ensure that the tension axis passed directly along the plane of the soldered joint between the two gold surfaces. The gold coupons were accurately machined from 2mm thick fine gold sheet to the final dimensions of 5mm by 10mm, using a very thin slitting disc.

Each gold coupon was bonded to its brass support with a proprietary silver solder which melted over the range 607 - 630°C. The silver solder was obtained in the form of a thin rod, which was rolled down to produce a sheet 0.1mm thick. The sheet was then cut into 5 x 10mm sections, which were placed between the gold coupons and the brass supports. Each assembly, which consisted of one half of the lap joint, was clamped in a small stainless steel vice and placed in a covered graphite crucible half-filled with charcoal. The crucible was then placed in a muffle furnace at 700°C for 30 minutes, removed and allowed to cool in air. No fluxing was necessary due to the reducing atmosphere

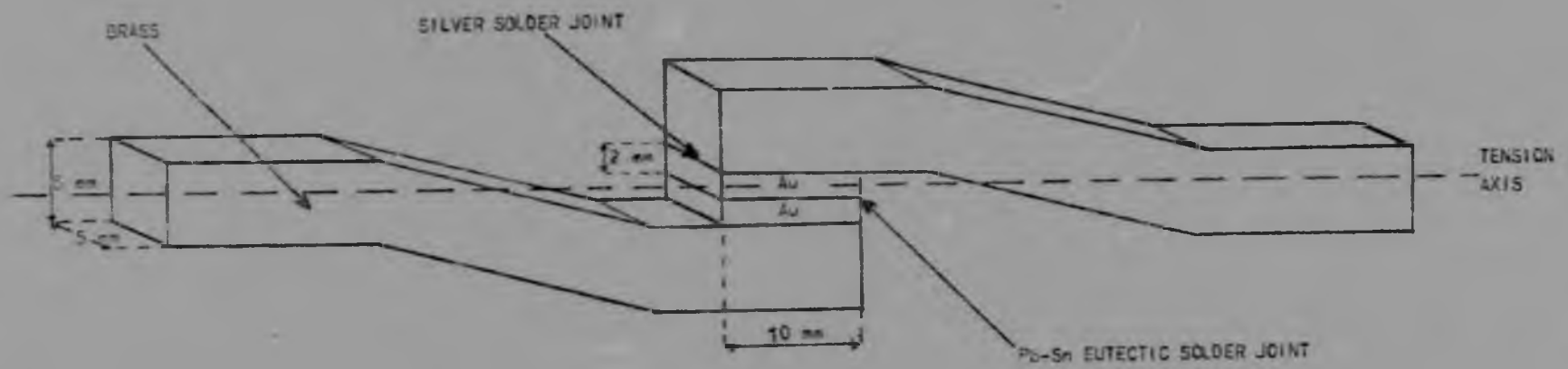


FIGURE 15 DIAGRAM OF LAP JOINT CONSTRUCTED FOR THE MEASUREMENT OF SHEAR STRENGTHS OF SOLDERED JOINTS BETWEEN PURE GOLD SURFACES.

inside the crucible.

Prior to the assembly of the lap joints, each composite was cleaned in nitric acid, the gold surface was lightly ground on 1000 grit water paper and etched by swabbing with aqua regia. They were then washed in distilled water, dried with alcohol and stored in a dessicator.

A preliminary series of lap joints were made up in order to determine the time required for soldering to take place, and to check the precision of the soldering method. Solder pre-forms, 0,1mm thick and 5mm wide x 10mm long were cut from a sheet of eutectic solder which had been manufactured from chemically pure tin and lead and rolled down to the required thickness. Each pre-form was etched with fluoroboric acid (HBF_4), rinsed and dried with alcohol. The lap-joints were assembled by placing a solder pre-form between the two gold surfaces which had been lightly coated with resin flux, incorporating two fine 0,1mm iron wires to maintain the joint spacing, and clamping the assembly in a small brass clamp which exerted pressure normally to the plane of the soldered joint.

The soldering operation was performed by introducing the clamped assembly into a salt bath maintained at the required temperature. The furnace used was the one which had been built for studying the dissolution of gold in molten solder (see Figure 11), except that the solder bath was replaced by a crucible containing a proprietary heat-treatment salt, which melted at approximately 150°C. Due to the dimensions of the crucible, the joint had to be introduced vertically, but capillary action prevented the molten solder from flowing out from between the gold surfaces.

A total of eight joints were prepared, all at an initial bath temperature of 200°C. The temperature of the bath fell by 10 to 20°C just after the joint assembly was introduced, but returned to the set

temperature within 60 seconds. It was also found that at least this length of time was necessary for soldering to occur and a final soldering time of 70 seconds after introduction of the joint was adopted for all of the following tests. After the joints had been removed from the salt bath, they were placed on an asbestos sheet and allowed to cool in still air to room temperature. The assembly was then placed in water to dissolve away adherent salt, and removed from the clamp.

The shear strengths of the joints were determined by testing them to destruction on a Hounsfield Tensometer. The lap joints were placed horizontally in the grips and stress was applied manually at a rate corresponding to a cross-head speed of approximately 3 mm per minute, until fracture occurred. A stress-strain graph was obtained for each specimen tested, and the fracture stress was recorded. This figure was divided by the area of the joint ($50mm^2$) and converted to megaPascals. The appearance of the fracture surface was noted and the fracture path was then determined by examination under the microscope. In order to do this, the projecting brass arms were cut off and the joint was mounted in plastic, lying on its side. The mounted specimen was ground and polished, and finally etched with nitric acid and acetic acid in glycerine. Diamond polishing paste was used, to minimise relief effects between the soft solder and the relatively hard gold.

In these preliminary tests, and in all of the subsequent ones, no plastic deformation of the joint was observed prior to failure. This was due to the design of the joint, which allowed no yielding of the solder film to occur due to the plastic constraint imposed upon it by the relatively massive, rigid gold side-pieces.

Of the eight joints tested, four were found to have high strengths

(17,4 to 20,5 mPa) and four to have low strengths (6,2 to 8,9 mPa).

Two factors were identified as being responsible for the low strengths of some joints. The first of these was inadequate wetting and incomplete bonding at the solder/gold interface. This was traced to the presence of a tenacious oxide film on t - solder foil, which was not removed by etching with HBF_4. To remove this film, it was necessary to rub the foil lightly with 1000 grit water paper and then polish the surface with a pad of filter paper which removed the final traces of oxide, producing a bright surface. This operation was performed immediately prior to assembly of the joints and a thin layer of resin flux was also used to ensure good wetting.

The second cause of low strength joints was inaccurate control of the joint spacing. It was noted from microscopic examination that the pressure exerted by the clamp, in order to hold the assembly together, forced the iron spacer wires into the soft gold surface, thus reducing the joint spacing to approximately 0,05 mm. During soldering, gold and tin from the solder reacted to form compound layers at each gold surface, and a lead-rich zone formed in the centre of the joint, between the compound layers. This zone was weak and the fracture was found to travel along it (see Plate 14).

To prevent this, a new clamp was constructed (see Plate 15). In this clamp, the two halves of the lap joint were held by cantilever arms which were located on a vertical column. No wire spacers were necessary since no force was applied across the joint, and thus the joint spacing was controlled by the thickness of the solder pre-form. Plate 16 shows a clamped joint assembly ready for soldering. The new clamp produced consistently spaced joints, and due to the higher proportion of solder in these joints, no continuous lead-rich zone was present in the centre.

(X 600)

Plate 14

Showing fracture in the central lead-rich zone between layers of columnar $AuSn_4$ crystals.

Plate 15

The brass clamp constructed to ensure accurate joint spacing.

Plate 16

Clamped joint assembly prior to soldering

The four high strength joints exhibited good wetting and a shiny, granular fracture surface. Microscopic examination revealed duplex $AuSn_2/AuSn_4$ compound layers at each gold/solder interface (see Plate 17), and acicular $AuSn_4$ crystals in the bulk of the solder. Some free lead was present adjacent to the compound layers, but the fracture propagated for the most part through the tougher lead-tin eutectic structure (see Plate 18).

This preliminary study led to the development of a satisfactory technique for the production and testing of gold-solder l p joints. It was now possible to proceed to the major investigation, which was to determine the effect of soldering temperature and time of ageing after soldering. Three soldering temperatures, 200, 220 and 240°C were selected, and two joints were also tested after soldering at 300°C. For each soldering temperature, two joints were to be tested in the as-soliered condition and two each after ageing at 100°C for one, two and three months. Accordingly, eight joints were made up at each temperature, following the experimental procedure developed during the preliminary study. A soldering time of 70 seconds was used at all four of the above temperatures. The ageing of the joints was done in a thermostatically controlled air oven at 100°C.

5.2.2. RESULTS AND DISCUSSION

The results obtained from this study are shown in Table 1. The precision in most cases was good, with only one set of results, those obtained for specimens aged for 30 days after soldering at 220°C, showing wide scatter. One of the results obtained after ageing a specimen which had been soldered at 200°C for 90 days was rejected, because virtually no wetting had occurred during soldering and the joint fractured immediately stress was applied.

Considering first the effect of soldering temperature upon the strength

Plate 17 (X 800)

Fractured specimen showing duplex compound layer, with $AuSn_2$ adjacent to the gold and columnar $AuSn_4$ adjacent to the solder.

Plate 18 (X 100)

High strength joint soldered at 200°C, showing fracture in the centre of the joint or in the lead-rich zone adjacent to the $AuSn_4$ layer.

TABLE 1 RESULTS OF SHEAR TESTS ON SOLDERED JOINTS BETWEEN PURE GOLD SURFACES.

	SOLDERING TEMPERATURE: 200°C			
AGEING PERIOD (DAYS)	0	30	60	90
SHEAR STRENGTH (mPa)	19,6 18,2	9,8 10,8	12,0 11,6	9,3 0*
	SOLDERING TEMPERATURE: 220°C			
AGEING PERIOD (DAYS)	0	30	60	90
SHEAR STRENGTH (mPa)	21,4 17,8	1,0 13,8 0,4	8,0 4,9	8,4 14,7
	SOLDERING TEMPERATURE: 240°C			
AGEING PERIOD (DAYS)	0	30	60	90
SHEAR STRENGTH (mPa)	23,6 27,7	19,6 18,2	21,8 20,0	15,6 9,3
	SOLDERING TEMPERATURE: 300°C			
AGEING PERIOD (DAYS)	0			
SHEAR STRENGTH (mPa)	37,4 38,3			

* DUE TO BAD WETTING - IGNORED.

of joints in the as-soldered condition, it can be seen that there was little difference between joints soldered at 200 and 220°C, but that those soldered at 240°C were of higher strength. This result is contradictory to expectations, and to the recommendation made by most investigators that soldering temperature be kept as low as possible. It was thought that a high soldering temperature would give rise to high concentrations of gold/tin intermetallic compounds in the joint, and hence would weaken the joint due to the inherent brittleness of the compounds. The concentration of intermetallic compounds did in fact increase as evidenced by Plates 18, 19 and 20, which depict joints soldered at 200, 220 and 240°C respectively. In those specimens soldered at 200 and 220°C there was still some free eutectic, while the joints soldered at 240°C exhibited complete reaction of the tin to form $AuSn_4$, the dark areas in the microstructure being free lead. Thus in the first two cases, the strength measured was essentially that of the lead-tin eutectic mixture while in the final case, it was that of $AuSn_4$ containing isolated pockets of free lead. The brittleness of the compound was not an important factor, since no plastic deformation of the solder layer could take place due to the constraint imposed by the design of the joint.

In order to study this phenomenon further, two joints were soldered at a temperature of 300°C, and these exhibited even higher strengths (see Table 1). It was noticed that the solder fillets on these specimens were hard and brittle. When some of this material was chiselled off and subjected to a fire assay, it was found to contain 51% by mass of gold.

The microstructures of the joints soldered at 200 and 220°C were essentially the same, the compounds present being $AuSn_2$ and $AuSn_4$ in each case. The $AuSn_2$ was in the form of a thin continuous layer adjacent to the gold surface, while the $AuSn_4$ was present as a layer of columnar crystals between the $AuSn_2$ layer and the solder, and as acicular or blocky

Plate 19 (X 300)

Joint soldered at 220°C. Note the increased proportion of $AuSn_4$, as compared with Plate 18.

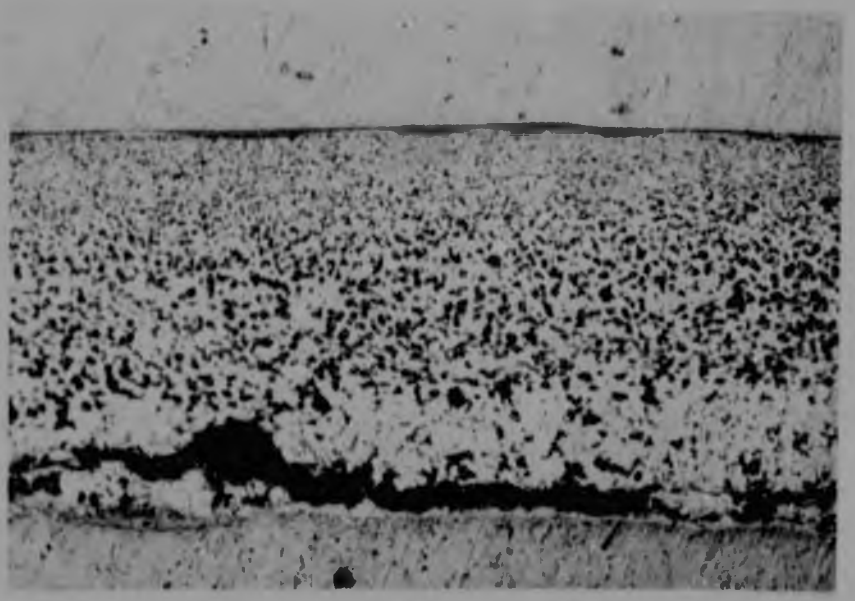


Plate 20 (X 300)

Joint soldered at 240°C. All of the tin has reacted to form $AuSn_4$. The dark areas are free lead.

crystals in the bulk of the solder fillet (see Plate 17, 18 and 19). The proportion of $AuSn_4$ was higher in the joints soldered at 220°C. The joints soldered at 240°C exhibited no free eutectic, all of the tin having reacted to form $AuSn_4$, but the $AuSn_2$ layer was still present at the gold surface (see Plate 21). The joints soldered at 300°C revealed a completely different microstructure (see Plate 22). In this case, dendritic AuSn was present, as well as $Au_{1}Sn_4$ and a second dark compound which is thought to be a gold-lead compound, since there was no free lead present in the joint.

All of these specimens exhibited a bright, silver fracture surface, similar to that shown in Plate 23. Microscopic examination revealed that in the joints soldered at 200°C, the fracture ran in the centre of the joint or in the lead-rich zone adjacent to the $AuSn_2$ layer (see Plate 18). In the case of the joints soldered at 220°C, the fracture ran either in the lead-rich zone (see Plate 19) or at the $AuSn_2/AuSn_4$ interface (see Plate 24). The joints soldered at 240°C fractured mainly at the $AuSn_2/AuSn_4$ interface or in the blocky $AuSn_4$ adjacent to it (see Plates 20 and 21).

After joints soldered at 200, 220 and 240°C had been aged at 100°C for 30 days, their shear strengths were measured (see Table 1). In every case the strengths were found to have decreased markedly. The two joints soldered at 220°C showed strengths of 1,0 and 13,8 mPa, and a third joint was prepared and aged in order to check these results. This joint had a shear strength of 0,4 mPa. It was noted that both of the very weak joints showed a completely dark, smooth fracture surface (see Plate 25) while the joint which had a strength of 13,8 mPa exhibited this type of fracture over approximately 40% of the surface (see Plate 26). The same type of fracture appeared also on the joints soldered at 200°C (see Plate 27) and to a lesser extent on those soldered at 240°C (Plate 28).

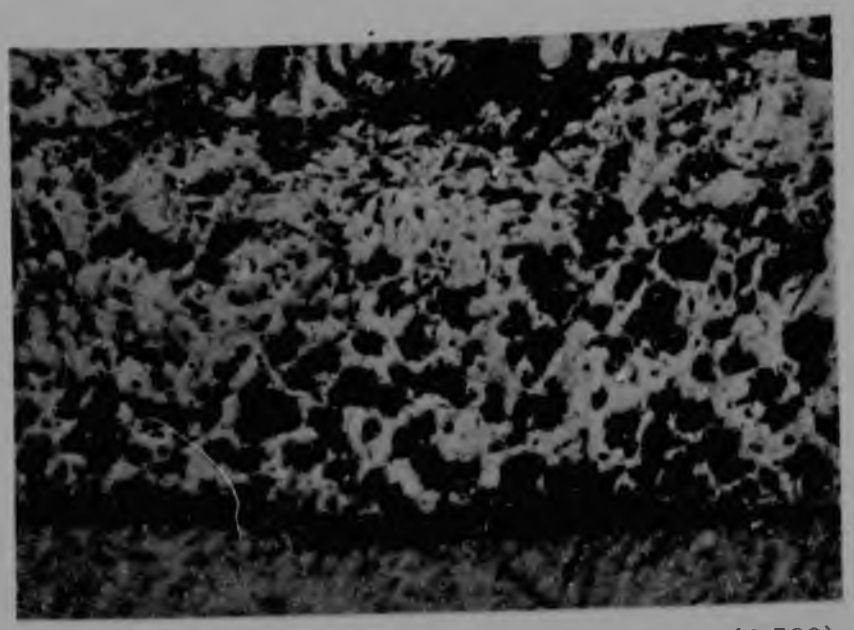


Plate 21 (X 700)

Joint soldered at 240°C. The continuous compound layer at the interface is $AuSn_2$.

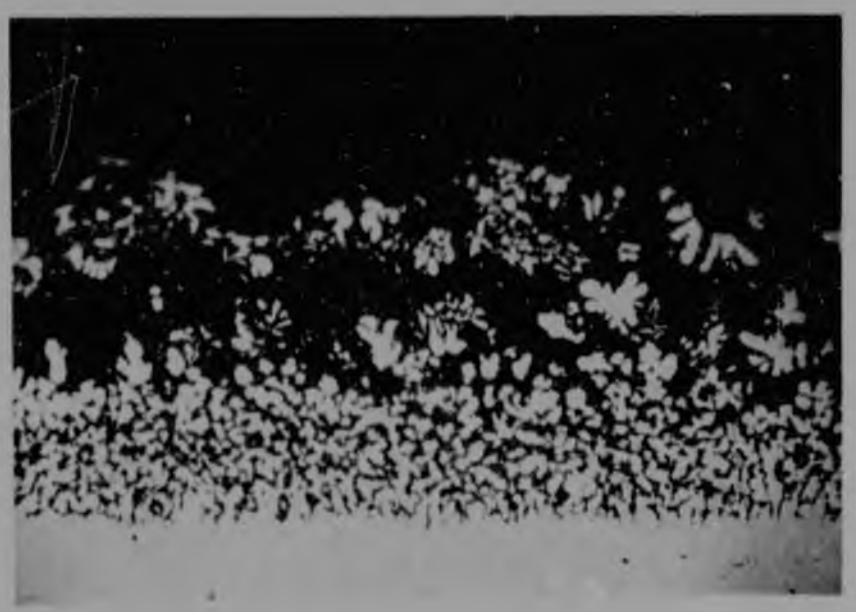


Plate 22 (X 300)

Joint soldered at 300°C, containing dendritic AuSn, with $AuSn_4$ and a possible gold-lead compound.

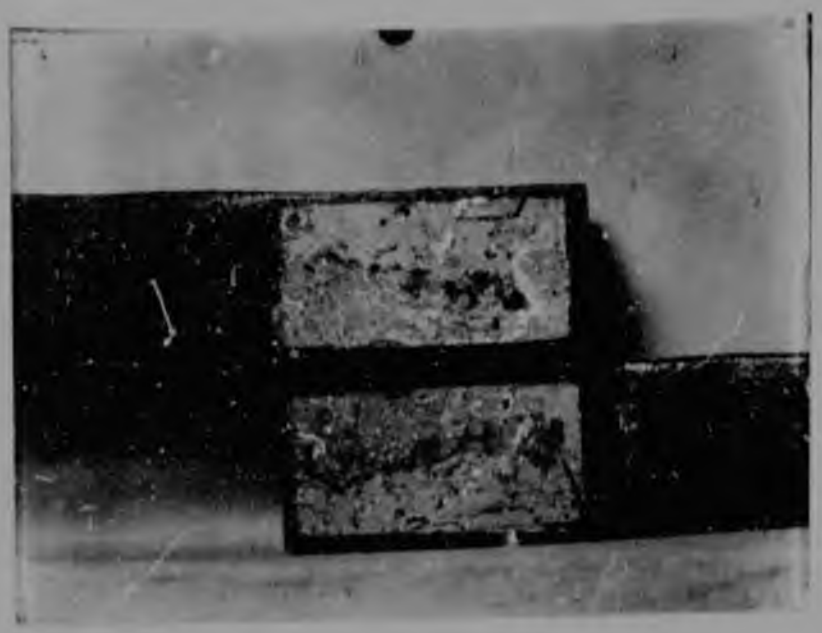


Plate 23

Joint soldered at 240°C. The bright fracture surface is typical of high strength joints.

Plate 24 (X 300)

Joint soldered at 220°C. The fracture has travelled at the $AuSn_2/AuSn_4$ interface in this area. Note the residual $AuSn_2$ on the gold surface.

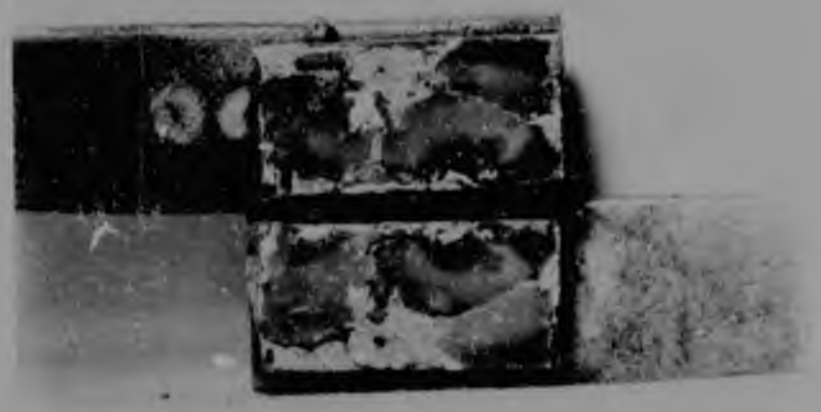


Plate 25

Joint soldered at 220°C and aged at 100°C for 30 days. Almost complete low strength, dark Au/$AuSn_2$ interface fracture.

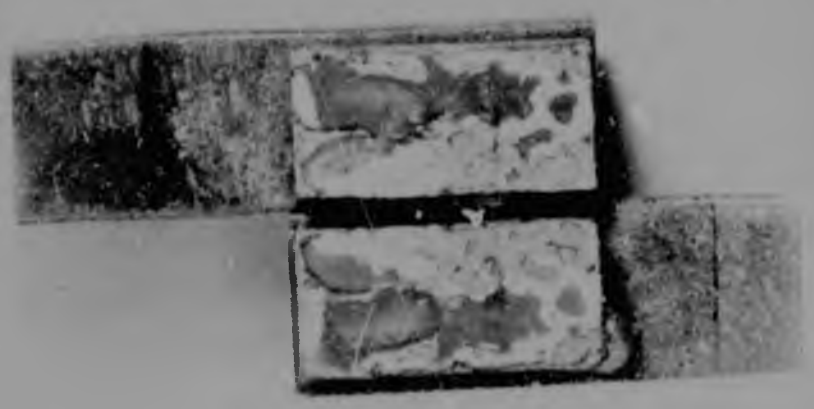


Plate 26

A second joint soldered at 220°C and aged for 30 days. The amount of dark interface fracture was lower than in 25 above and the joint was correspondingly stronger.

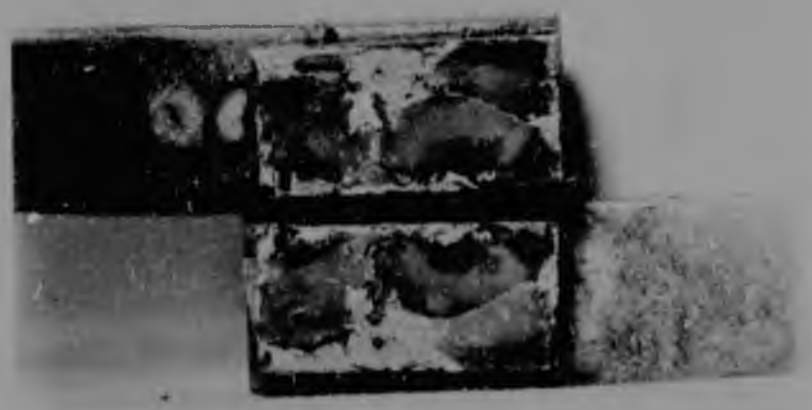


Plate 25

Joint soldered at 220°C and aged at 100°C for 30 days. Almost complete low strength, dark Au/$AuSn_2$ interface fracture.

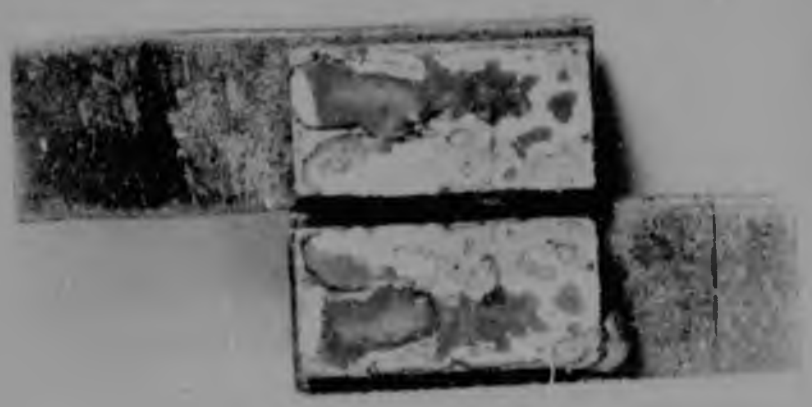


Plate 26

A second joint soldered at 220°C and aged for 30 days. The amount of dark interface fracture was lower than in 25 above and the joint was correspondingly stronger.

Plate 27

Joint soldered at 200°C and aged for 30 days. The dark fracture surface covers approximately 40% of the total area.

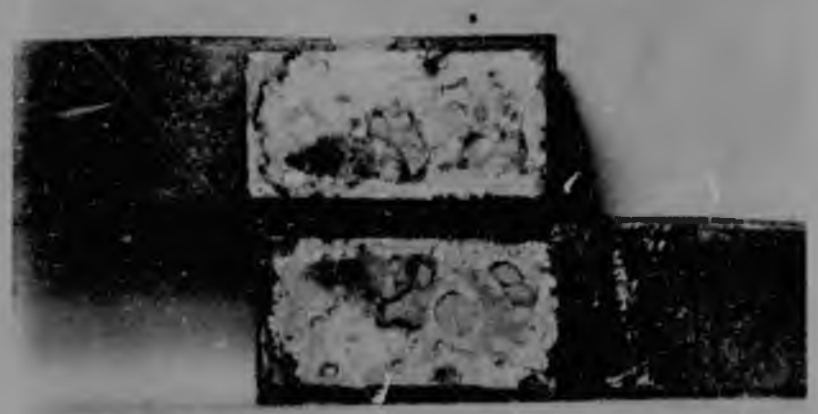


Plate 28

Joint soldered at 240°C and aged for 30 days. The proportion of dark fracture surface is low.

Microscopic examination revealed that these dark areas were the result of separation at the gold/$AuSn_2$ interface (see Plate 29). It was also apparent that the $AuSn_2$ compound layer in particular had increased greatly in thickness, from 2 - 3 microns after soldering to approximately 30 microns after ageing for one month. This ten-fold increase can be readily seen by comparison of Plate 17 with Plate 29.

The bright areas on the fracture surfaces were associated either with fracture through the centre of the joint or at the $AuSn_2/AuSn_4$ interface (see Plate 30). The joints soldered at 200°C exhibited all three fracture types, those soldered at 220°C were predominantly of the $Au/AuSn_2$ interface type and those soldered at 240°C were mainly of the $AuSn_2/AuSn_4$ interface type.

The results obtained from lap joints which had been aged for sixty days at 100°C revealed slight increases in strength over those aged for only thirty days (see Table 1). The joints soldered at 220°C were again lower in strength than those soldered at 200 and 240°C. Once again, the fracture surfaces of the 220°C joints were almost completely dark and smooth, corresponding to separation at the $Au/AuSn_2$ interface. The proportion of dark fracture surface was also seen to have increased on the other specimens (see Plates 31, 32, 33) compared with those which had been aged for only 30 days (see Plates 25, 26, 27, 28).

Microscopic examination revealed that the joints soldered at 200°C exhibited three types of fracture, namely in the centre of the joint, at the $AuSn_2/AuSn_4$ interface and at the $Au/AuSn_2$ interface, in approximately equal proportions. Those soldered at 220°C fractured predominantly at the $Au/AuSn_2$ interface, with small areas in the centre of the joint, and those soldered at 240°C fractured predominantly in the centre. The $AuSn_2$ compound layers in the joints soldered at 200 and 220°C had grown further to approximately 40 microns in thickness, while in the joints

Plate 29 (X 170)

Soldered at 220°C and aged for 30 days. Growth of the compounds has occurred, leading to separation at the Au/$AuSn_2$ interface. This area corresponds to the dark fracture surface.

Plate 30 (X 150)

Soldered at 200°C and aged for 30 days. Separation at the $AuSn_2$/$AuSn_4$ interface, corresponding to the bright fracture surface.

Plate 31

Soldered at 200°C and aged for 60 days. Note increased proportion of dark Au/$AuSn_2$ interface fracture.

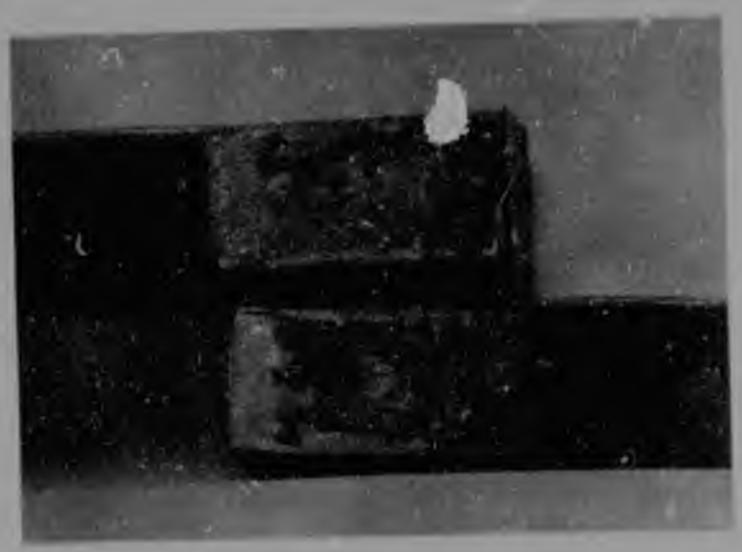


Plate 32

Soldered at 220°C and aged for 60 days. Almost total separation at the Au/$AuSn_2$ interface.

Plate 33

Soldered at 240°C and aged for 60 days. The proportion of dark fracture surface has increased in comparison with plate 28.

Plate 34

Soldered at 200°C and aged for 90 days. Note increased proportion of dark fracture surface.

Plate 35

Soldered at 220°C and aged for 90 days. Total separation at the Au/$AuSn_2$ interface has occurred.

Plate 36

Soldered at 240°C and aged for 90 days. Once again the proportion of dark fracture has increased.

soldered at 240°C, they remained at approximately 20 microns. This was due to a lack of free tin in the joint, since it had all reacted to form either $AuSn_4$ or $AuSn_2$ by this time.

After ageing for 90 days, the original soldering temperature had little effect on the shear strength of the joints, these all falling in the range 8,4 to 15,6 mPa. The joints soldered at 200 and 240°C had decreased in strength while those soldered at 220°C had increased. Once again the fracture surfaces revealed increased areas of dark interface separation (see Plates 34, 35, 36).

The joints soldered at 200 and 220°C exhibited further growth of the $AuSn_2$ layer to approximately 50 microns, while those soldered at 240°C showed no further growth of the compound layer, with separation at the centre of the joint predominating in these specimens.

5.2.2.1. SCANNING ELECTRON MICROSCOPE STUDIES OF THE FRACTURE SURFACES

It was felt that the use of a scanning electron microscope with the capacity to analyse small areas would be of great value in studying the fracture surfaces obtained after testing soldered lap joints. Such an instrument was kindly made available by the Chamber of Mines of South Africa, and the results obtained are discussed below.

The first specimen studied was one which had been soldered at 200°C and aged for 30 days at 100°C. The area of interest was a dark, smooth area at the centre of the specimen. At low magnification this was seen to be a flat area surrounded by steep walls rising to another flat, plateau-like surface (see Plate 37). Analysis of the lower surface revealed this to be gold, while the plateau area gave strong responses for both gold and tin. Unfortunately the analysis was not quantitative, but the smoothness of this surface indicates that it is the top of the the $AuSn_2$ compound layer. Thus this was an area where the fracture had

Plate 37 (X 130)

S.E.M. photograph showing an area where the fracture had jumped from the $AuSn_4/AuSn_2$ interface (left hand side) to the $Au/AuSn_2$ interface (centre).

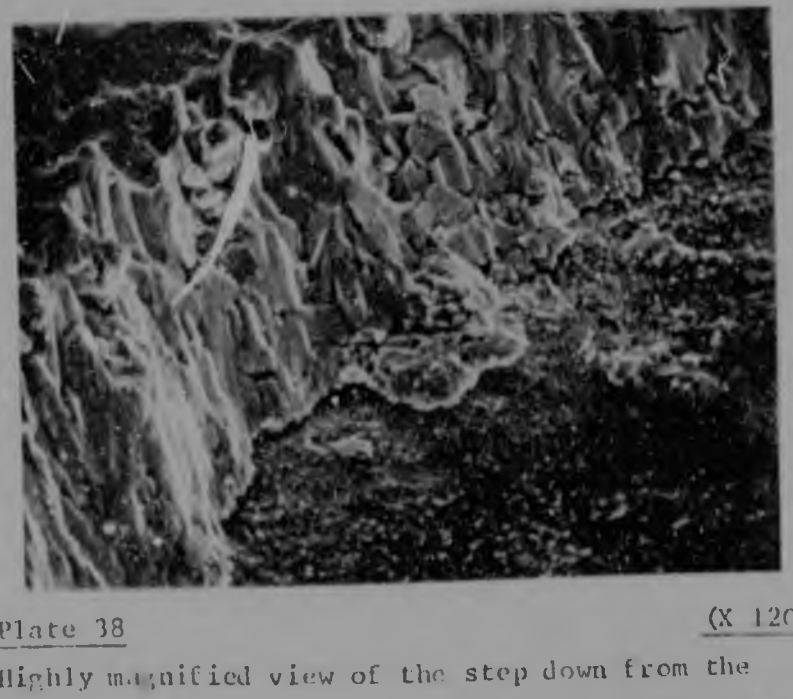


Plate 38 (X 1200)

Highly magnified view of the step down from the $AuSn_4/AuSn_2$ interface to the $AuSn_2/Au$ interface.

Plate 22 (X 30)

Low power view showing all three types of fracture.

travelled along the $AuSn_4/AuSn_2$ interface and then crossed the $AuSn_2$ interface. A view of this step at high magnification is shown in Plate 38. The brittle nature of the $AuSn_2$ layer can be seen from the many cracks in it, and the clean separation between the $AuSn_2$ and the gold is also apparent.

A second specimen, which had been soldered at 200°C and aged for 60 days was then studied. Plate 39 shows an area of the specimen where all three types of fracture had occurred. The plateau at the top of the picture is the surface of the $AuSn_2$ layer, i.e. in this area fracture took place along the $AuSn_4/AuSn_2$ interface. The flat area running diagonally across the picture from the top right-hand corner is the gold surface, the fracture having run along the $AuSn_2/Au$ interface in this area. Below this area on the right-hand side, the fracture reverted to the $AuSn_4/AuSn_2$ interface, producing another small plateau. The rough, dimpled areas in the bottom left quarter are those where the fracture progressed through the centre of the joint above the $AuSn_4$ compound layer, producing a typical dimpled ductile fracture surface.

5.2.3. CONCLUSIONS

The following conclusions can be drawn from the results obtained in this investigation.

a) For the type of joint studied, the shear strength increases with soldering temperature. This increase can be attributed to a higher proportion of hard, strong intermetallic compound in the joint. However, the compound is very brittle and the impact resistance of the joints will be low.

b) Ageing of the joints at 100°C after soldering produced an overall decrease in strength, after three months, of between 35 and 50%, depending upon the initial soldering temperature.

c) The decrease in shear strength after ageing was associated with the

appearance of smooth, dark areas on the fracture surface. It was noted that the weakest joints exhibited the greatest proportion of this type of fracture. The dark fracture surface was found to correspond to areas where separation at the Au/$AuSn_2$ interface had occurred.

d) Growth of the $AuSn_2$ compound layer occurred during ageing, and this growth led to separation between the $AuSn_2$ and the gold. This can be attributed to shear stresses set up at the Au/$AuSn_2$ interface during growth of the $AuSn_2$, and to mismatch between the crystal lattices of the face-centred cubic gold and the orthorhombic $AuSn_2$. From lattice spac... data, it can be calculated that a 3% volume increase occurs when gold and tin react to form $AuSn_2$, and this may lead to stresses at the interface.

e) The growth rate of the $AuSn_2$ layer was lower in the specimens soldered at 240°C than in those soldered at 200 and 220°C. This was because most of the tin in the solder had reacted with gold during soldering and less free tin was available for compound formation during ageing. Thus the onset of loss of strength due to separation at the Au/$AuSn_2$ interface was delayed, but after 90 days ageing, the strengths had fallen to much the same level as those of the other joints.

5.3 TESTS ON JOINTS BETWEEN GOLD-PLATED SURFACES

5.3.1. EXPERIMENTAL WORK

It was decided to undertake a further study to determine the effect of ageing upon the tensile properties of soldered joints between the types of gold-plated surfaces normally encountered in industrial applications. Three types of gold plate were selected, and two of these were studied both with and without a nickel underplate. Two thicknesses of gold plate, representing the practical minimum and maximum, were used in the study.

The types of gold plate required were not available in South Africa,

and therefore the Forschungsinstitut für Edelmetalle und Metallchemie in Swäbisch-Gmünd, West Germany were approached by the Chamber of Mines. This institute is deeply involved in the field of gold-plating and very kindly agreed to supply the required specimens. On their recommendations, three types of gold were selected as being representative of those used for the plating of printed circuit boards. These were:

1) A hard gold from a citric acid solution containing $KAu(CN)_2$ at a pH of approximately 3. This gold contained 0,3 to 0,4 mass per cent cobalt, and was also produced under the necessary conditions to ensure that it contained organic polymer material, such as that identified by Munier[11].
2) Gold from a cyanide free electrolyte, consisting of a gold-sulphite complex, at a pH of approximately 9.
3) Gold from an alkaline cyanide bath containing $KAu(CN)_2$ at a pH of 10 or higher. This plate was produced so as to be free of organic material.

The gold was plated onto copper substrates, and in the cases of types 1 and 3, a second set of specimens was provided with a 5 to 7 micron under layer of electroless nickel deposited from a Watt's bath. All three types were provided in two thicknesses, namely 3 and 10 microns. 3 microns is the practical minimum necessary to ensure good corrosion resistance and solderability, while 10 microns is the approximate maximum thickness for economic reasons.

The procedure for the manufacture of soldered lap joints was essentially the same as that used in the study of joints made between bulk gold surfaces, described in an earlier section of this chapter. It was, however, no longer necessary to use composite test pieces, since the copper substrate onto which the gold was plated provided the necessary load-bearing capacity.

The specimens obtained from Germany were in the form of 50 by 30 mm. tough pitch copper plates, 3 mm. in thickness. Each plate was plated with gold on one side for a length of 15 mm. along with 50 mm. side (see Figure 16). A total of twenty such plates were received, broken down according to the plating schedule below:

No of Plates	Type of Au Bath	Thickness of Au layer, (microns)
2	1	3
2	1	10
2	2	3
2	2	10
2	3	3
2	3	10
2*	1	3
2*	1	10
2*	3	3
2*	3	10

* With a 5 to 7 micron Watt's nickel underplate

Each plate was machined to produce five strips 5 mm. wide by 50 mm. long, resulting in ten strips of each distinct type. Thus five lap joints could be made in each category and it was decided to test one of these in the as-soldered condition, two after ageing at 100°C for 30 days and two after ageing for 60 days.

The lap joints were constructed by clamping two strips together with a 5 by 10 mm, 0,1 mm. thick solder foil between the gold surfaces, as described previously, and then immersing the clamped assembly in a salt bath at the required temperature. A soldering temperaure of 220°C was used for all of the specimens, and due to their lower mass, the soldering

FIGURE 16 Gold-Plated Copper Sheet, as received from Germany, before cutting into five mm. strips.

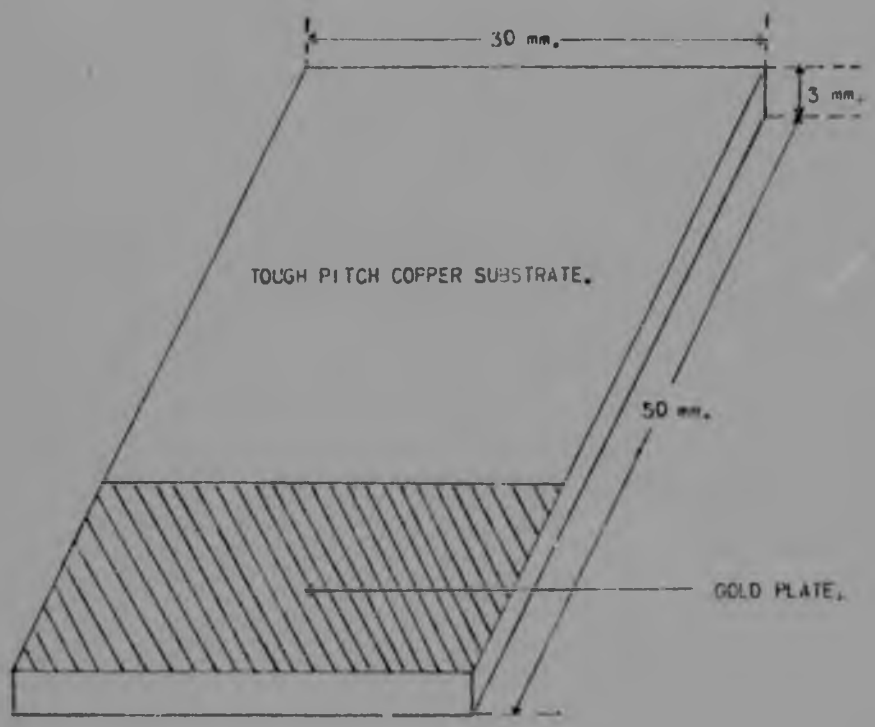
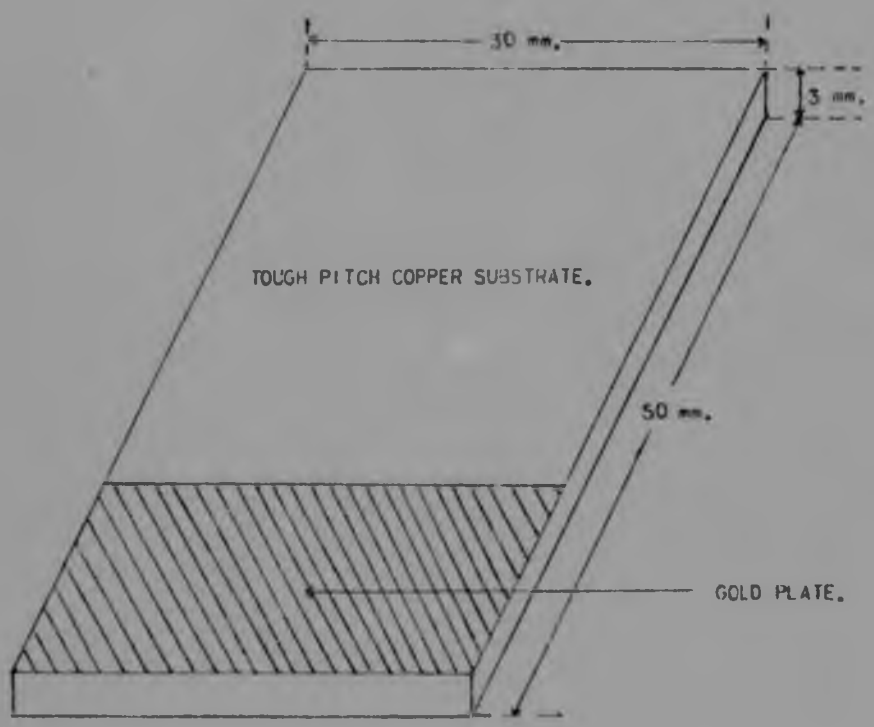


FIGURE 16 Gold-Plated Copper Sheet, as received from Germany, before cutting into five mm. strips.



time was reduced from seventy to sixty seconds. The gold-plated surfaces were not etched prior to soldering, but were swabbed with trichloroc-thylene, rinsed with alcohol, and dried.

After soldering the specimens were removed from the clamp and either tested in the as-soldered condition or aged at 100°C in an air oven. The shear strengths were measured on a Hounsfield Tensometer, and a stress-strain curve was obtained for each specimen. The appearance of each fracture surface was noted, and microscopic examination was used to determine the path followed by the fracture.

5.3.2. RESULTS AND DISCUSSION

The results obtained from the whole study are shown in Table 2. Three important conclusions can immediately be drawn from these, namely:

a. In every case, ageing at 100°C reduced the shear strengths of the joints, and the loss of strength increased with increase in ageing time.

b. The strengths of joints made between ten micron thick gold-plated surfaces were in every case inferior to those of joints between three micron gold-plated surfaces.

c. The presence of a nickel under-plate was detrimental to joint strength.

The type of gold plate selected had a profound effect upon the strength of the soldered joint. The results obtained for specimens plated with acid cyanide gold (bath 1) were very low and several of the joints were found to have separated under no applied stress, during the ageing treatment.

The first five specimens in this group exhibited shiny, granular fracture surfaces and were found to have failed in the centre of the joint (see Plate 40). Most of the gold-plate had dissolved during soldering and therefore compound growth during ageing was limited. Some growth did take place however, (see Plates 41 and 42) and the specimen

TABLE 2 RESULTS OF SHEAR TESTS ON SOLDERED JOINTS BETWEEN GOLD-PLATED SURFACES.

No.	Bath Type	Thickness of Gold Plate (microns)	Nickel Substrate	Polymer	Ageing Period (Months)	Joint Strength (mPa)	Nature of Fracture
1	1	3	No	Yes	0	9,8	Bright, in centre or adjacent to $AuSn_4$ layer
2	1	3	No	Yes	1	2,9	Bright, in centre of joint.
3	1	3	No	Yes	1	0	Bright, in centre of joint.
4	1	3	No	Yes	2	1,3	Bright, in centre of joint.
5	1	3	No	Yes	2	0,4	Bright, in centre or at $AuSn_2$/Cu interface.
6	1	10	No	Yes	0	0	Dark, at $AuSn_2$/Au interface.
7	1	10	No	Yes	1	0	Dark, at centre or at $AuSn_4$/$AuSn_2$ interface.
8	1	10	No	Yes	1	0	Dark, at $AuSn_2$/Au interface.
9	1	10	No	Yes	2	0	Dark, at $AuSn_2$/Au interface.
10	1	10	No	Yes	2	0	Dark, at $AuSn_2$/Au interface.
11	1	3	Yes	Yes	0	2,3	Bright, in centre or at $AuSn_2$/Ni interface.
12	1	3	Yes	Yes	1	0	Bright, in centre or at $AuSn_2$/Ni interface.
13	1	3	Yes	Yes	1	4,0	Bright, adjacent to $AuSn_4$ or at $AuSn_2$/Ni interface.
14	1	3	Yes	Yes	2	0	Bright, in centre or at $AuSn_2$/Ni interface.
15	1	3	Yes	Yes	2	0	Bright, in centre or at $AuSn_2$/Ni interface.
16	1	10	Yes	Yes	0	0	Bright, in centre and dark, at $AuSn_2$/Ni interface.
17	1	10	Yes	Yes	1	0	Dark, at $AuSn_2$/Au interface
18	1	10	Yes	Yes	1	0	Bright, in centre and dark at $AuSn_2$/Au interface.
19	1	10	Yes	Yes	2	0	Bright, in centre and dark at $AuSn_2$/Au interface.
20	1	10	Yes	Yes	2	0	Dark, at $AuSn_2$/Ni interface.
21	2	3	No	No	0	22,7	Bright, adjacent to $AuSn_4$ or at $AuSn_4$/$AuSn_2$ interface.
22	2	3	No	No	1	20,8	Bright, adjacent to $AuSn_4$ or at $AuSn_4$/$AuSn_2$ interface.
23	2	3	No	No	1	12,0	Bright, adjacent to $AuSn_4$ or at $AuSn_4$/$AuSn_2$ interface.
24	2	3	No	No	2	14,2	Bright, adjacent to $AuSn_4$ or at $AuSn_4$/$AuSn_2$ interface.
25	2	3	No	No	2	16,0	Bright, adjacent to $AuSn_4$ or at $AuSn_4$/$AuSn_2$ interface.
26	2	10	No	No	0	19,5	Bright, adjacent to $AuSn_4$ or at $AuSn_4$/$AuSn_2$ interface.
27	2	10	No	No	1	14,2	Bright, adjacent to $AuSn_4$ or at $AuSn_4$/$AuSn_2$ interface.
28	2	10	No	No	1	14,2	Bright, adjacent to $AuSn_4$ or at $AuSn_4$/$AuSn_2$ interface.
29	2	10	No	No	2	12,9	Bright, in centre of joint.
30	2	10	No	No	2	13,8	Bright, in centre of joint.
31	3	3	No	No	0	28,1	Bright, in centre or adjacent to $AuSn_4$ layer.
32	3	3	No	No	1	14,7	Bright, in centre or at $AuSn_4$/$AuSn_2$ interface.
33	3	3	No	No	1	20,5	Bright, in centre or at $AuSn_4$/$AuSn_2$ interface.
34	3	3	No	No	2	15,6	Bright, in centre or at $AuSn_4$/$AuSn_2$ interface.
35	3	3	No	No	2	19,3	Bright, in centre or at $AuSn_4$/$AuSn_2$ interface.
36	3	10	No	No	0	20,9	Dark, at $AuSn_4$/$AuSn_2$ or adjacent to $AuSn_4$ layer.
37	3	10	No	No	1	10,7	Dark, at $AuSn_2$ interface.
38	3	10	No	No	1	3,1	Dark, at $AuSn_2$ interface.
39	3	10	No	No	2	7,6	Dark, at $AuSn_2$ interface.
40	3	10	No	No	2	0	Dark, at $AuSn_2$ interface.
41	3	3	Yes	No	0	1,91	Bright, adjacent to $AuSn_4$ or $AuSn_4$/$AuSn_2$ interface.
42	3	3	Yes	No	1	8,5	Dark, at $AuSn_2$/Ni interface.
43	3	3	Yes	No	1	5,3	Dark, at $AuSn_2$/Ni interface.
44	3	3	Yes	No	2	2,7	Dark, at $AuSn_2$/Ni interface.
45	3	3	Yes	No	2	6,2	Dark, at $AuSn_2$/Ni interface.
46	3	10	Yes	No	0	18,7	Bright, in centre and at $AuSn_4$/$AuSn_2$ interface.
47	3	10	Yes	No	1	3,1	Dark, at $AuSn_2$/Au interface
48	3	10	Yes	No	1	2,5	Dark, at $AuSn_2$/Au interface
49	3	10	Yes	No	2	3,1	Dark, at $AuSn_4$/$AuSn_2$ or $AuSn_2$/Au interface.
50	3	10	Yes	No	2	2,7	Dark at $AuSn_2$/Au or $AuSn_2$/Ni interface.

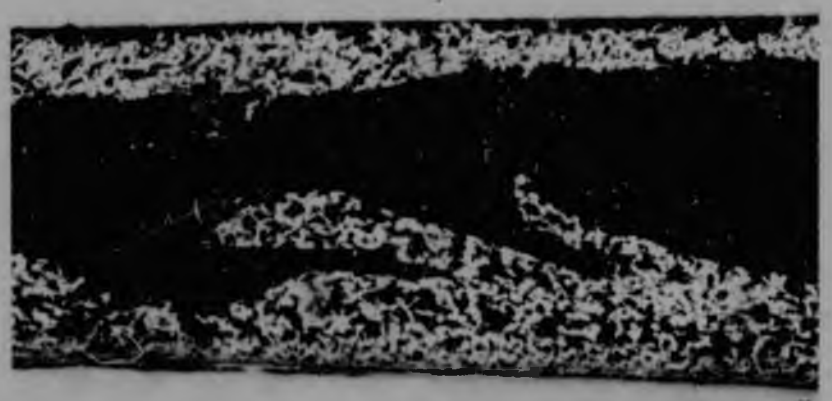


Plate 40 (X 200)

Specimen no. 1, showing failure in the centre of the joint.

Plate 41 (X 170)

Specimen no. 2. Note the growth of the $AuSn_2$ layer after ageing for 30 days.

Plate 42 (X 150)

Specimen no. 5, showing growth of $AuSn_4$ and failure in the lead-rich zone between the $AuSn_4$ layers. Note also the porosity in the joint.

which had been aged for sixty days was found to have fractured in the lead-rich zone between the columnar $AuSn_4$ crystals which had grown from each side of the joint. All five of the specimens exhibited considerable porosity due to gas evolution during soldering.

Specimens 5 to 10 were all very weak, either failing before any measurable load was applied or separating during the ageing treatment. These all exhibited dark, smooth fracture surfaces (see Plate 43) similar to those obtained in the investigation on bulk gold surfaces (see Plate 35).

Microscopic examination revealed that there was a layer of residual gold, approximately 5 microns in thickness, remaining on the surface of the copper substrate. The dark fracture surface was found to correspond to separation at the interface between the $AuSn_2$ compound layer and the residual gold (see Plate 44). Specimen 7 showed some separation in the centre of the joint, corresponding to the bright area on the fracture surface in Plate 43 . Both modes of fracture are shown in the photomicrograph, Plate 45. Considerable growth of the $AuSn_2$ layer occurred during ageing, producing a final layer approximately 20 microns in width.

Specimens 11 to 15 correspond to numbers 1 to 5 except that they had a 5 to 7 micron nickel under-layer. These joints also produced bright fracture surfaces and separation was found to have occurred in the centre of the joint (see Plate 46). All of the gold had dissolved and there was a layer of columnar $AuSn_4$ crystals adjacent to the nickel surface. The aged specimens revealed small areas where fracture had occurred between the nickel and the $AuSn_4$ layer.

Specimens 16 to 20 were once again extremely weak, and revealed either partial or complete dark $AuSn_2$/Au interface fractures (see Plate 47). As in the case of specimen numbers 6 to 10, there was a residual layer of gold, and growth of the $AuSn_2$ layer adjacent to this occurred during ageing

Plate 43

Srecimens 7 (top) and 8 (bottom). Dark fracture surfaces of low strength joints.

Plate 44 (X 250)

Specimen no. 6. Complete separation between the $AuSn_2$ layer and the residual gold.

Plate 45 (X 130)

Specimen no. 7, showing both fracture in the centre of the joint and separation at the Au, $AuSn_2$ interface.

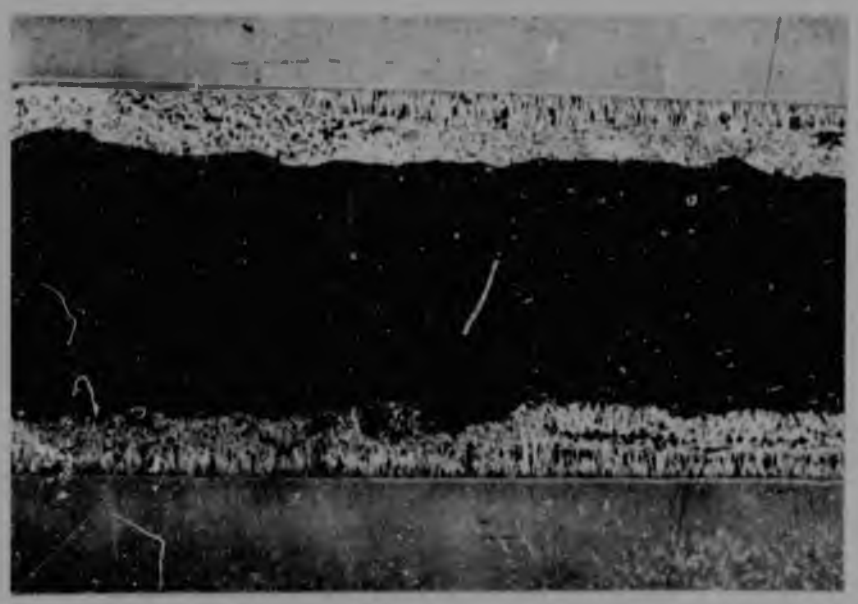


Plate 46 (X 130)

Specimen no. 11. Note the columnar $AuSn_4$ crystals from each surface and fracture in the zone between them. The nickel underlayer is visible between the copper substrate and the $AuSn_4$ crystals.

Plate 47

Specimens 17 (top) and 18 (bottom). Partial or complete $AuSn_2$/Au fractures.

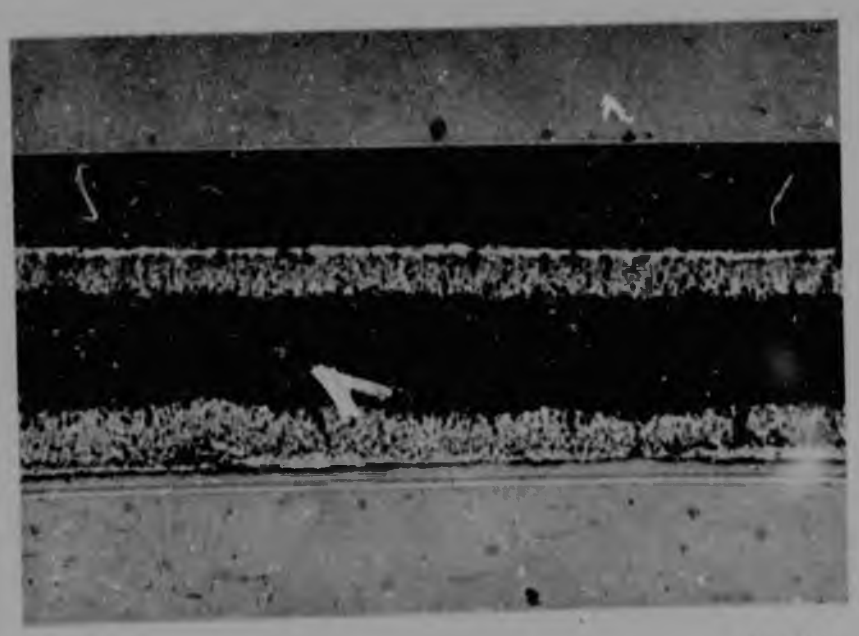


Plate 48 (X 170)

Specimen no 19. Note growth of $AuSn_2$ and separation both at the Au/$AuSn_2$ interface and in the centre of the joint. The nickel underlayer is also visible.

(see Plate 48). The bright areas on the fracture surfaces were found to correspond to separation in the centre of the joint.

Specimens 21 to 25 were plated with a 3 micron layer of gold from a sulphite bath (bath 2). These joints were much stronger than those plated in the acid cyanide bath, although there was a significant decrease in strength as the time of ageing at 100°C increased. All of these joints gave bright, granular fracture surfaces, such as is shown in Plate 49. Under the microscope, the fracture was seen to have occurred either adjacent to the $AuSn_4$ layer or at the $AuSn_4/AuSn_2$ interface (see Plate 50). The mode of fracture did not change with ageing, but some compound growth and a general coarsening of the structure was apparent (see Plate 51), and this was probably responsible for the decrease in strength.

Specimens 26 to 30, that is those plated with 10 microns of gold from the sulphite bath, were generally weaker than those with a 3 micron sulphite gold layer (specimens 21 to 25), due to the increased proportion of gold-tin compounds in the solder fillet. Once again, there was a decrease in shear strength with ageing at 100°C. The specimens all exhibited bright, granular fracture surfaces, corresponding to separation in the lead-rich zone adjacent to the $AuSn_4$ layer, or in the centre of the joint, as in the case of 21 to 25 above. There was a residual gold layer, and growth of the $AuSn_2$ layer adjacent to this occurred during ageing. The decrease in shear strength after ageing can once again be attributed to coarsening of the structure.

The specimens plated with a 3 micron layer of gold from the alkaline cyanide bath (numbers 31 to 35), showed high shear strengths. Specimens 32 and 34 were found to exhibit bad wetting of the gold by the solder, and thus gave low values. The lack of wettability of this type of gold plate was to prove a problem in this study. Specimens plated in baths 1 and 2 soldered readily, but those from bath 3, although soldered

Plate 49

Specimens 22 (top) and 23 (bottom). Bright fracture surfaces of high strength joints.

Plate 50 (X 130)

Specimen no. 21. Separation at the $AuSn_4/AuSn_2$ interface or adjacent to the $AuSn_4$ layer.

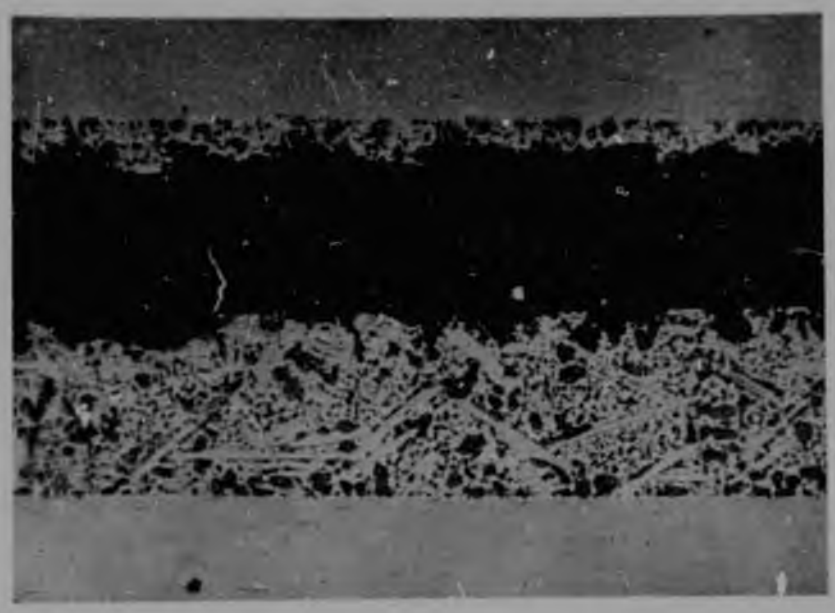


Plate 51 (X 130)

Specimen no. 25. Some growth of the compounds and considerable coarsening of the structure has occurred during the ageing treatment. (cf. Plate 50)

according to the same procedure revealed a significant degree of non-wetting in approximately half of the specimens.

Specimens 31 to 35 all exhibited a bright fracture surface, and separation was found to have occurred both in the centre of the joint and at the $AuSn_4/AuSn_2$ interface (see Plate 52).

The shear strengths of specimens 36 to 40, i.e. those having a 10 micron alkaline cyanide plate, were very severely reduced by ageing at 100°C. Number 36 produced a high strength fracture adjacent to the $AuSn_4$ layer or at the $AuSn_4/AuSn_2$ interface but the specimens which were aged all exhibited typical dark fracture surfaces, corresponding to separation at the $Au/AuSn_2$ interface (see Plate 53). The presence of residual gold enabled considerable growth of the compound layers to occur leading to separation at this low-strength interface.

The shear strength of specimen 41 was high, and the fracture was found to have occurred either at the $AuSn_4/AuSn_2$ interface, or adjacent to the columnar $AuSn_4$ layer, giving a bright fracture surface. The strength was lower than that of specimen 31, which had the same thickness (3 microns) of alkaline cyanide gold, but was without a layer of nickel beneath the gold. The joints in this category which had been aged, however, yielded low shear strengths, and produced dark, smooth fractures at the $AuSn_2/Ni$ interface, shown in Plates 54 and 55. The lack of complete wetting of the gold surface can also be seen in these photographs.

Specimens 46 to 50 revealed the same decrease in shear strength, together with the corresponding change in fracture mode, upon ageing. Growth of the $AuSn_2$ layer was seen to have occurred on ageing and this led to complete separation at the interface between the $AuSn_2$ layer and the gold which remained after soldering. A typical dark smooth interface fracture surface is shown in Plate 55.

Plate 52 (X 100)

Specimen no. 33. Separation has occurred in the centre of the joint and at the $AuSn_4/AuSn_2$ interface.

Plate 53 (X 250)

Specimen no. 39. The presence of residual gold has enabled growth of the $AuSn_2$ layer to occur, causing separation at the $Au/AuSn_2$ interface.

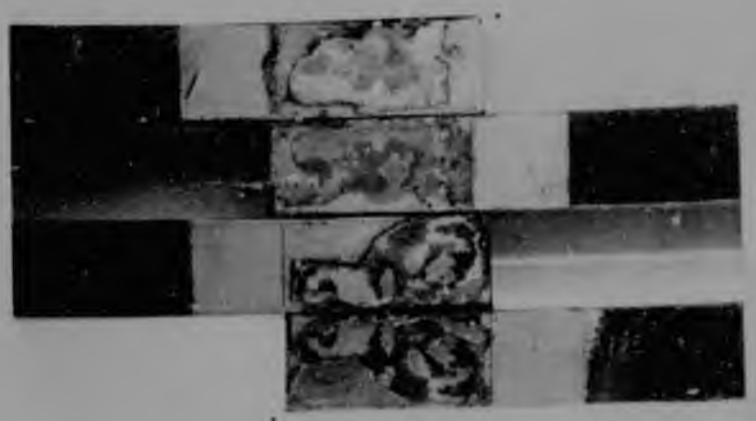


Plate 54

Specimens 42 (top) and 43 (bottom). Low strength, dark fractures at the $AuSn_2$/Ni interface. Note also the incomplete wetting of the gold by the solder.

Plate 55

Specimens 45 (top) and 49 (bottom). Typical dark fractures corresponding to separation at the $AuSn_2$/Au interface after growth of the $AuSn_2$ during ageing.

5.3.3. CONCLUSION

From the results of the tests performed, the following conclusions can be drawn:

a. Operation of soldered connections between gold plated surfaces at moderately elevated temperatures for extended periods is detrimental to the strength of the connections.

b. The decrease in joint strength is associated with the growth of gold-tin intermetallics, particularly $AuSn_2$, leading to separation at the gold/$AuSn_2$ interface and producing a typical dark, smooth fracture surface.

c. The use of thick gold plate should be avoided, since these joints were invariably weaker than those made with thin gold plate. The thick gold plate did not all dissolve during soldering, and this enabled massive growth of the gold-tin compounds to occur during the ageing treatment.

d. The presence of a nickel under-layer is detrimental to joint strength.

e. Gold from an acid cyanide bath should be avoided for applications involving soldering. The very low strengths of joints made with this type of gold plate may be due to the presence of an organic polymer, although no direct evidence for this was found. It was noted that these joints contained considerable porosity, possibly due to the production of gases as a result of decomposition of the polymer during solder.

f. The best results were obtained with a 3 micron layer of gold from an alkaline cyanide bath, without a nickel underlayer. The solderability of this type of gold deposit was poor however, the solder failing to wet the gold completely in several cases. The results obtained with a 3 micron layer of gold from a sulphite bath were almost as good however, and the solderability of this type of gold plate was excellent.

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