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Compound growth in platinum/tin–lead solder diffusion couples

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The two types of reactions that occur between 60/40 tin–lead solder and platinum were explored: (1) solid-state diffusion, in which the intermetallic compound $PtSn_4$ was observed to form; and (2) dissolution. Both bulk and thin-film couples were used and the extent of reaction in each was revealed by optical and scanning electron microscopy methods. Solid-state compound growth followed parabolic kinetics with an effective activation energy of 23 kcal mol^{-1} (96.2 kJ mol^{-1}). Diffusion of platinum through $PtSn_4$ appears to limit compound growth. Dissolution of platinum wires in solder resulted in a linear decrease in wire diameter with time. The process occurred with an activation energy of 20.4 kcal mol^{-1} (85.4 kJ mol^{-1}) and was attributed to Pt–Pt bond breaking assisted by strong chemical interaction with tin.

1. Introduction

1.1. Background

Soldering is an important joining operation used in the manufacture of electronic devices and assemblies. Frequently, metallization layers are applied to substrates and chip components to provide surfaces suitable for soldering. When a circuit metallization layer is connected to other conductors by a soldering operation, the solder must metallurgically bond with the base material. The solder must wet the surface and dissolution reactions with the base metal are inevitable. Compounds may form at the interface and be adherent to the surface; alternately, adhesion, can be destroyed and compounds dispersed in the molten material. A low rate of dissolution implies that the base material will be stable during the soldering operation.

Interest in compound formation does not end with the melting process. After solidification, solid-state reactions, such as the growth of intermetallic compound layers, can occur. Compounds which form between solders and the metallization can yield mechanically and electrically unreliable connections after exposure to elevated temperatures during initial burn-in and accelerated testing [1], or during service. Because these interfacial compounds may affect the strength of the joint, a study of the kinetics of compound formation between metallization layers and solder is important for reliability concerns. A recent conference has addressed and reviewed many of the scientific and engineering issues of solder mechanics in interconnection and packaging technology [2].

In the present study the use of platinum as a base metal or metallization layer on integrated circuits was explored, and its reactions with the widely used 60 Sn–40 Pb solder measured in both the liquid and solid states. In particular the following information was sought: (a) composition and morphology of reaction products; (b) kinetics of dissolution of platinum in molten solder; (c) kinetics of solid-state diffusion; (d) activation energies for diffusion and dissolution; and (e) mechanisms for the processes of diffusion and dissolution.

1.2. Review of prior research

Prior research on the Pt/Sn–Pb system is meagre. A search of the literature in *Diffusion and Defect Data* [3] over a 15 yr period yielded no references in either solid or liquid states, and only one reference on the subject of metal dissolution in Pb–base solders. In their study of gold, silver, copper and nickel wires in Pb–5 Sn and Pb–5 In–2.5 Ag solders, Berg and Hall [4] found that nickel had the lowest rate, and gold had the highest rate of dissolution in the range 360–500 °C. They also observed that dissolution followed an Arrhenius relation and that the rate-determining step involved diffusion away from the metal/solder boundary.

Bader [5] measured the rate of dissolution of platinum in a 60 Sn–40 Pb solder between 371 and 482 °C and his results will be discussed later in the context of the present work. Although his work was an exhaustive determination of dissolution rates of various metals (gold, silver, copper, nickel and palladium) in solder, a shortcoming was the absence of microchemical characterization of the reactions. In a later study, Bader researched both the dissolution and solid-state

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reactions between palladium and 60 Sn–40 Pb solder in a comprehensive way [6]. Linear and parabolic intermetallic compound growth kinetics were observed paralleling the behaviour of platinum reported in the present investigation.

Two additional studies that involved reactions between a solid and a liquid metal are those of Zakraysek [7] (Cu/60 Sn–40 Pb) and Kang and Ramachandran [8] (Ni/Sn). In both cases the data were insufficient to yield consistent growth rates as a function of temperature. In addition, the analyses, were limited, rendering these works of peripheral interest to the present study.

Tu and Rosenberg [9] found that platinum formed intermetallic compounds with both tin and lead, even at room temperature. In their X-ray diffraction study of room-temperature interdiffusion in bimetallic thin films, a layer of tin or lead was individually reacted with a second layer of copper, silver, gold, nickel, palladium or platinum. In each case an intermetallic compound was formed. Surprisingly, in all cases only one compound formed even though the phase diagrams indicate the existence of more than one thermodynamically stable compound at room temperature.

2. Experimental procedure

2.1. Materials, sample preparation and thermal treatment

2.1.1. Solid-state diffusion in the bulk

Thermocouple-grade platinum wire with a purity of > 99.95% and nominal 0.5 mm (0.020 in.) diameter, was used in bulk-reaction experiments. The platinum wires were degreased in a commercially available solvent containing CCl_4. They were fluxed in an aqueous solution of 90% ZnCl–10% NH_4Cl and then dip coated in a solder bath maintained at 200 °C to ensure complete wetting. The coated wires were then placed on the axis of cylindrical moulds and solder was cast around the wires to produce rod specimens. The molten solder temperature was 196–200 °C and the castings solidified in 15–20 s. Results from the dissolution studies show that negligible compound growth occurs during the preparation period. Rod specimens were cut into 6 mm lengths and exposed to diffusional temperatures between 125 and 178 °C. The higher temperature was only 5 °C below the melting point of the solder at this composition. Ageing times ranged from 1 week to 5 months.

2.1.2. Dissolution experiments (bulk platinum)

The platinum wires were cut into samples approximately 70 mm long, degreased in CCl_4 and fluxed in an aqueous solution of zinc and ammonium chlorides. They were then mounted in a fixture that allowed samples to be immersed in the solder bath to a reproducible depth of about 50 mm during the dissolution treatment.

The solder bath was prepared by melting 1634.4 g Sn and 1089.6 g Pb in an electrolytic iron crucible. The purity of both metals exceeded 99.97%. The crucible was placed in a vertical tube furnace which was controlled by a chromel–alumel thermocouple immersed in the melt. During dissolution experiments, temperatures from 485–535 °C were held within ± 1 °C of the nominal value. The large volumes of tin and lead ensured that the concentration of any platinum compounds in the melt remained negligible.

An oxide skin that formed on the surface of the bath was skimmed off prior to immersion of each sample. Immersion times ranging from 2–300 s were determined with a stop watch and were accurate to ± 1 s. Upon removal, each sample was quenched in water at room temperature.

2.1.3. Dissolution of thin platinum films in coatings of solder and tin

To simulate more closely solder conditions in microelectronics, composite thin-film specimens were prepared. These consisted of sequentially deposited layers of platinum (1 μm thick) and either pure tin or 60 Sn–40 Pb (25 μm thick), all on an oxidized silicon wafer. The specimens were then vacuum reflowed at temperatures of 250 ± 5 °C for times up to 2500 s.

2.2. Metallographic sample preparation

Metallographic preparation of these materials is extremely difficult. The process can best be described as trying to obtain a plane surface on a cross-section of a piece of metal embedded in chewing gum. Special procedures had to be developed in order to overcome the difficulties encountered. The conventional methods for the preparation of solder samples are completely ineffective in preparing platinum, because they rely heavily on chemical polishing to delineate the tin- lead rich phases. Conversely, platinum preparation methods are far too aggressive for the preparation of the solder, and promote severe damage to the grain structure.

Sample preparation techniques are described in detail elsewhere [10]. Here a brief summary of the important steps and considerations is itemized.

(a) Specimen mounting in slow-curing epoxy. Slow curing is necessary to minimize specimen heating during mounting and eliminate voids and porosity. Voids trap abrasives, creating surface scratches, and absorb etchants which stain prepared surfaces.

(b) Grinding on automatic polisher. Some 15 stages of grinding employing SiC abrasive grit sizes ranging from 320–4000 (FEPA European standard) with grinding loads of 50–100 N and grinding times for 20 and 25 s, were used. Rounding at the platinum solder interface and retention of abrasive particles in the solder matrix are key concerns.

(c) Final polishing. Vibratory polishing employing 1 μm alumina and 0.05 μm colloidal silica (Syton) completed the specimen preparation.

Obtaining a cross-sectional view of the silicon wafer containing the platinum/solder and Pt/Sn films also posed a challenge, and some rounding of the metal/silicon interface was unavoidable. Polishing was done manually because of the small size and delicate

nature of the specimens but the procedure used was very similar to that of the wire samples. A hard wax rather than metallographic epoxy was used for more precisely adjustable mounting.

2. 3. Analytical methods

2.3.1. Optical microscopy

When the compound layer thickness was greater than 5 μm, optical metallography was employed. A Neophot metallograph provided an image of the sample which was projected into a television camera. Measurements were recorded with a digital thickness gauging system.

At least five measurements were taken on each of the solid-state diffusion samples at equally spaced intervals around the circumference of each wire. The compound-layer thickness varied from less than 1 μm to over 30 μm, and was measured at a magnification of X1000. Examples of both thick and thin compound layers are shown in Fig. 1a and b.

For the dissolution experiments, measurements were made using the same optical microscope described above. Many diameter determinations were made from several cross-sections on each wire in order to obtain reliable data from these samples. Each datum represents the average of nine or more diametrical measurements taken from two or three different cross-sections on each sample. The difficulty in obtaining accurate measurements arises because the amount of platinum removed from the radius of the wire is of the order of 10 μm, but the diameter of the wire is about 500 μm. The entire cross-section must be in view in order to measure the diameter on the video monitor, and a magnification of X125 or less was required. The problem is compounded if the axis of the wire is not exactly perpendicular to the polished end and, therefore, the samples were held in a fixture during mounting to minimize this possibility.

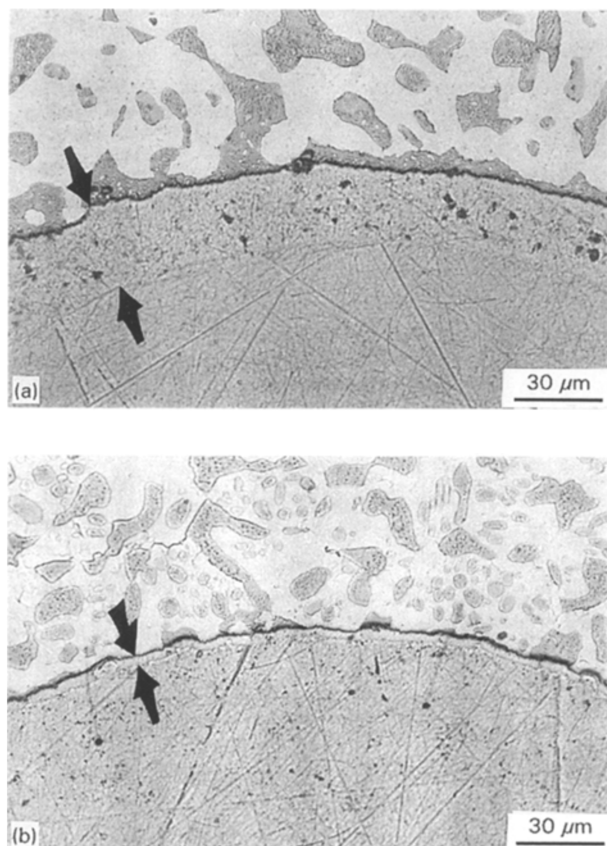
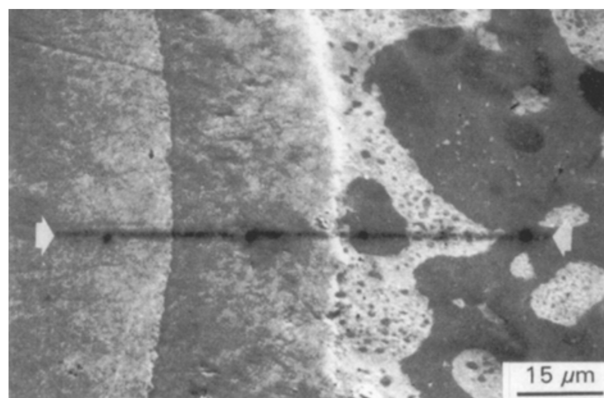


Figure 1 (a) Optical micrograph of a sample diffused 122 days at 170 °C. Arrows indicate compound width. (b) Optical micrograph of a sample diffused 122 days at 125 °C.

2.3.2. SEM and X-ray methods

In most cases measurements by optical microscopy were appropriate, as confirmed by scanning electron microscopy (SEM). It was found, however, that for layer thicknesses below about 5 μm the compound layer was not clearly defined. Therefore, SEM/EDX (energy dispersive X-ray analysis) was employed to determine both the composition and thickness of the compound layers. This involved X-ray analysis at individual points as well as line-scan analyses across regions of the prepared surface. An example of the use of line profile analysis is shown in Fig. 2. The black



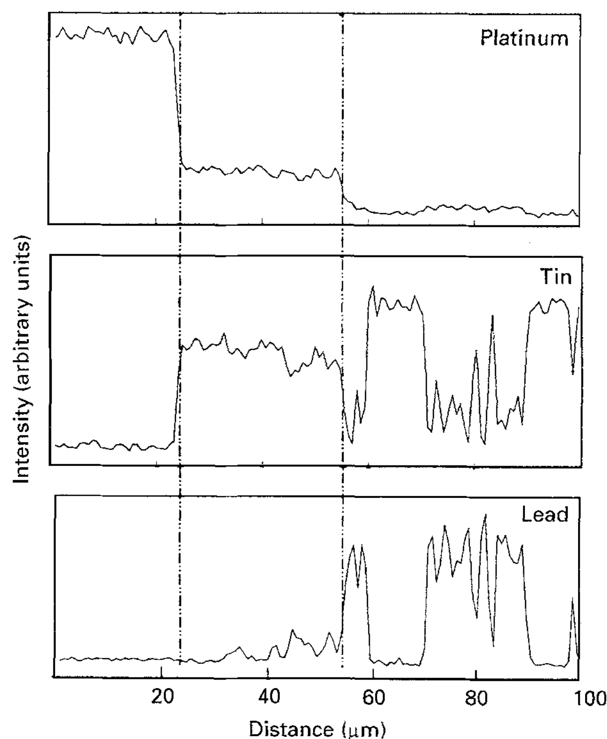


Figure 2 Scanning electron micrograph and corresponding X-ray line, relative concentration profiles for platinum, tin and lead. Specimen diffused at 170 °C for 122 days.

line across the micrograph is a carbonaceous surface deposit formed by interaction of the electron beam with residual hydrocarbons in the system. The line gives an unambiguous indication of the region analysed. Comparison of the elemental line scans show that the compound layer on this sample starts 24% of the way across the scanned area, and ends 56% of the way across. Because the scanned line is 89 μm long, the compound layer is found to be 28.5 μm thick at this stage.

3. Results

3.1. Solid-state diffusion experiments

The composition of the intermetallic compound was analysed by EDX methods and found to be $PtSn_4$. This finding is consistent with the observations of Brothers [11]. In Fig. 3 the compound thickness is plotted against the square root of ageing time. The slopes of these plots are related to the solid-state growth rates for the temperatures indicated and their magnitudes were obtained from a least-squares-regression analysis. None of the growth rate lines intersect the origin, suggesting that an incubation time period is required to initiate compound growth.

3.2. Dissolution experiments

It is interesting that the morphology of the first material to form in the bulk dissolution samples after only a few seconds is identical to that which forms after a long time. Consider Fig. 4a (485 °C, 2 s) and b (535 °C, 90 s). They are quite similar even though their temperature–time histories are different. For the long exposure time of 300 s at 485 °C, some spalling of the compound on the wire surface occurred. It is believed that this spalling exposed fresh platinum metal to the solder bath leading to anomalously high dissolution in this time period. It also contributed to the large deviation of the statistical average. Results of the dissolution experiments yielded diameter reductions which

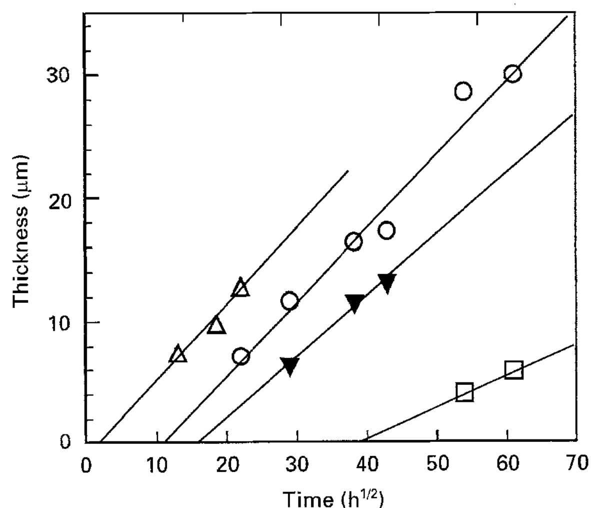


Figure 3 Intermetallic compound growth kinetics for platinum–tin–lead solder solid-state diffusion couples. Data are plotted as compound thickness versus square root of time. (□) 125 °C, (▼) 150 °C, (○) 170 °C, (△) 178 °C.

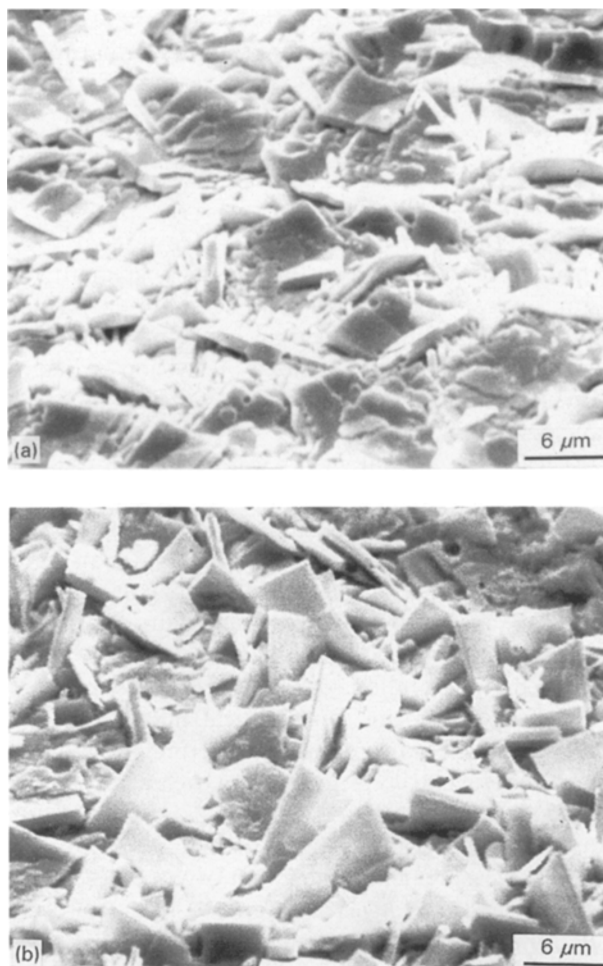


Figure 4 Scanning electron micrographs of (a) 485 °C, 2 s dissolution specimen, and (b) 535 °C, 90 s dissolution specimen.

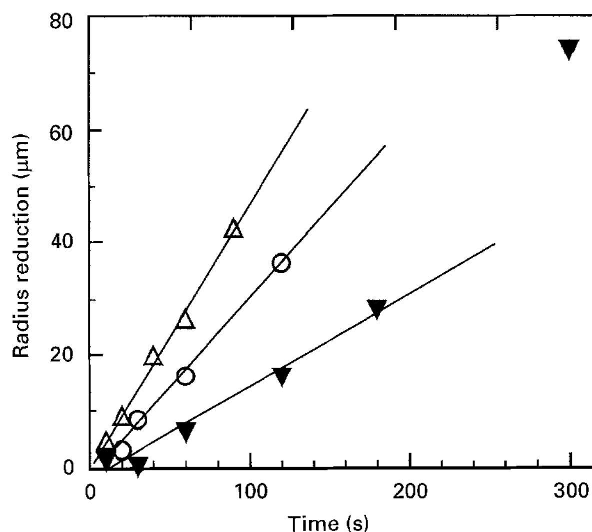
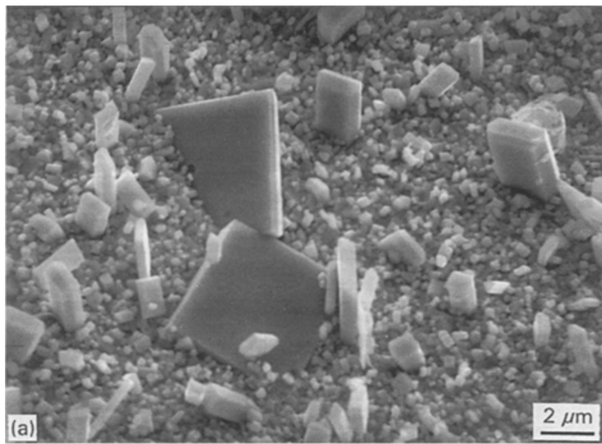


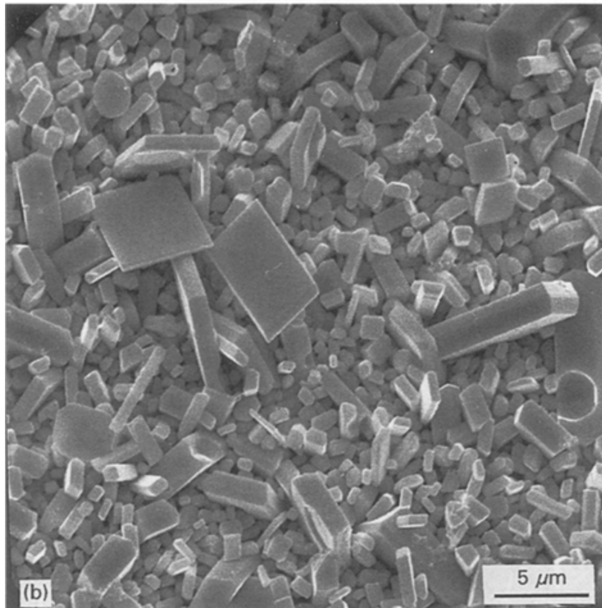
Figure 5 Dissolution kinetics of platinum in molten tin–lead solder. Data are plotted as reduction in wire radius versus time. (▼) 485 °C, (○) 573 °C, (△) 535 °C.

were converted to radius reductions. The data are plotted in Fig. 5, revealing the linear relation between material removed and reaction time.

3.3. Thin-Film dissolution

The irregular nature of the $PtSn_4$ crystals and their large size relative to the total platinum and tin





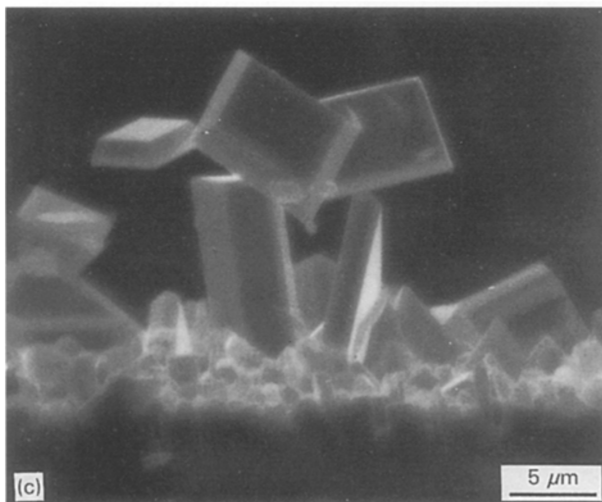


Figure 6 SEM images of platinum/tin–lead solder thin-film couples: (a) reflowed at 500 °C for 2 s (tin solder, plan view); (b) reflowed at 253 °C for 2500 s (tin–lead solder, plan view); (c) reflowed at 253 °C for 2500 s (tin solder, cross-sectional view).

thicknesses prevent us from deriving quantitative information from these experiments. However, some qualitative conclusions can be drawn. The structure of the Pt/60 Sn–40 Pb specimens strongly resembled the structure of the Pt/Sn specimens, with the main difference being a reduction in the size of the large $PtSn_4$ crystals. A similar structure and growth rate would be expected, because the transfer of tin through the liquid solder to the intermetallic surface appears to be too rapid to be the limiting step; also lead does not appear to form intermetallics.

Fig. 6a shows a Pt/Sn film specimen, reflowed at 500 °C for 2 s, which may be compared to Fig. 4a. The large $PtSn_4$ crystals appear to grow more perfectly on the thin-film specimen, but are about the same size as those in the bulk specimen. Fig. 6b shows a Pt/60 Sn–40 Pb thin-film specimen reflowed at 253 °C for 2500 s. Some lead remains on the surface after chemical removal of the solder. The fine-grained structure between the large crystals is more clearly seen in the thin-film specimens. Fig. 6c shows the intermetallic layer in cross-section, reflowed at 253 °C for 2500 s. The intermetallic layer is composed of very large faceted crystals surrounded by a densely packed collection of independent smaller crystals; only $PtSn_4$ was found to exist in this layer. The faint white line across the bottom of the film is the remaining platinum over an SiO_2 film on the silicon substrate.

The seemingly suspended $PtSn_4$ crystals may be the result of high levels of dissolved platinum in the liquid tin relative to levels in the bulk melts.

4. Discussion

4.1. Solid-state diffusion experiments

In the metallurgical literature, compound-growth kinetics are usually modelled by a formula of the type

$$X_s = K(Dt)^{1/2} \quad (1)$$

where X_s is the thickness, D is the diffusion coefficient and the constant K depends upon relevant concentrations but is independent of temperature. This $(Dt)^{1/2}$ dependence stems from the analysis of a planar rather than a cylindrical diffusion couple, but the change in radius due to dissolution in this study is sufficiently small that the planar relation applies. A comparison of solutions for non-steady- state diffusion in planar and cylindrical tube geometries of bimetallic layers was performed by Khandros and Ohring [12]. They found that the two solutions for the diffusivity differed by only 0.35% when the tube thickness was $0.2r_0$, where r_0 is the outer tube radius. The error in D obtained by assuming a planar diffusion couple in the present study is estimated to be much smaller. This is due to the fact that the initial radius was 250 μm and the thickest compound layer formed was no more than 30 μm, or $0.12r_0$ in any of the samples that were prepared.

The activation energy for compound growth is contained in D, i.e.

$$D = D_0 e^{-Q_s/RT} \quad (2)$$

where Q_s is the activation energy for diffusion and D_0 is the usual pre-exponential factor.
Combining these two equations we obtain

$$X_s = A e^{-Q_s/2RT} t^{1/2} \quad (3)$$

where A is the product of K and $D_0^{1/2}$. Clearly, the effective activation energy determined from the slope

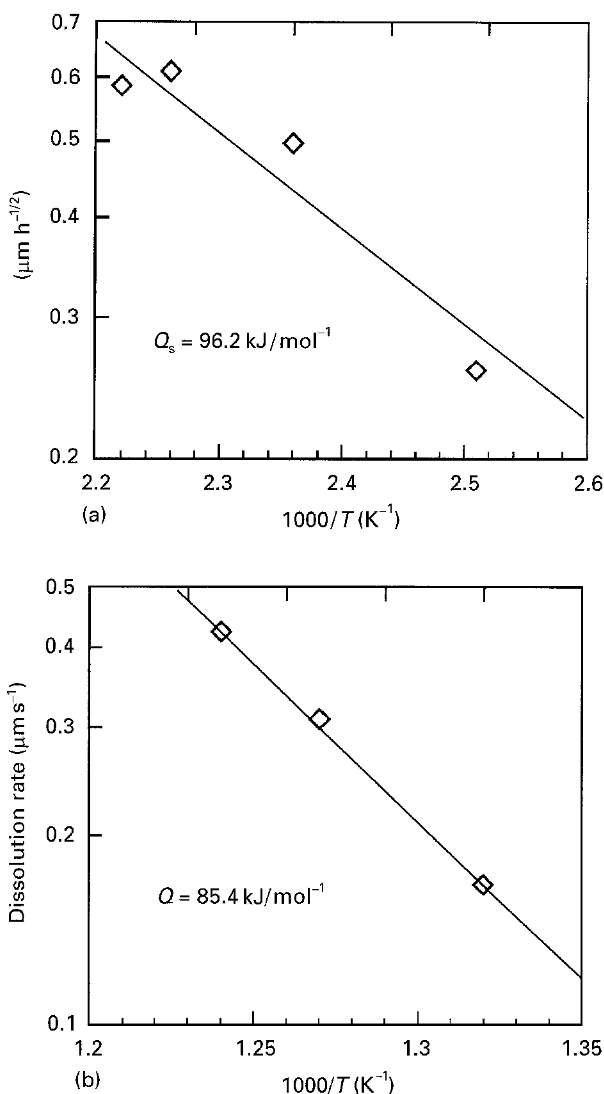


Figure 7 Arrhenius plots of (a) $PtSn_4$ compound growth, and (b) dissolution kinetics

of the Arrhenius plot of Fig. 7a is equal to $1/2Q_s$, and therefore $Q_s = 23$ kcal mol^{-1} (96.2 kJ mol^{-1}).

This value for Q_s should be viewed in the context of solid-state interdiffusion of platinum or tin in the involved matrices of Sn–Pb and $PtSn_4$. The rate-limiting step in the growth of the compound apparently involves diffusion of either platinum or tin through $PtSn_4$, and therefore, Q_s is most likely attributable to atomic migration in this matrix. Unfortunately, interdiffusion data for $PtSn_4$ do not exist for comparison. What is available, however, are interdiffusion data for metals in lead and tin matrices as well as in Sn–Pb solders. A compilation of values for assorted metals in these matrices is given in Table I. For comparison, diffusion data for elements in platinum are also tabulated.

With respect to diffusion of elements in group IV matrices, it should be noted that anomalous fast interstitial diffusion is possible. Noble metals silver, gold and copper, as well as palladium, are known to be fast diffusers. It is highly probable that platinum is also a fast diffuser. Typical fast diffusion activation energies have a magnitude that is half those obtained in this study. It would, therefore, appear that such

TABLE I Activation energies for diffusion of elements in solvent elements lead, platinum and tin [13–15] (temperature ranges are not shown, and values are given in kcal/mole)

	Activation energy (kcal mol^{-1})		
Solute Elements	Pb	Pt	Sn
Ag	14.4	61.7	15.3
Al		46.3	
Au	9.8	60.2	14.4
Cd	21.2		27.9
Co	11.1	74.2	22.0
Cu	8.0		7.9
Fe		58.2	
Hg	22.7		26.1
In	26.8		25.7
Ir	10.6		
Na	28.3		
Ni	10.6		
Pb	25.5		
Pt	10.1	67.3	
Sb	22.2		29.2
Sn	23.8		25.2
Ti	24.3		14.7
Zn	11.4		11.8

a mechanism plays little role in compound growth. It is not known whether fast diffusion of platinum occurs in $PtSn_4$.

Activation energies for substitutional diffusing atoms in tin and lead are typically 23 kcal mol^{-1}, a value which is closer to the magnitude of Q_s measured here. Again, lack of data for $PtSn_4$ prevents definitive conclusions to be drawn on operative transport mechanisms. Nevertheless, neither fast diffusion nor grain-boundary migration are suggested by the diffusion systematics.

Trends in Table I suggest that the most likely mechanism for interfacial movement involves compound growth at the compound/solder interface rather than at the platinum/compound interface. The argument is based on (a) the high energy required for any species in the compound layer to diffuse into platinum, and (b) the low energy required for species in the compound layer to diffuse into solder. From these considerations it is concluded that layer growth occurs by the movement of platinum atoms from the surface of the wire through the intermetallic compound and their subsequent reaction with tin to form $PtSn_4$. Kirkendall marker experiments could resolve the question of the mobile species.

Analysis of the data collected by Bader [6] on the behaviour of palladium/solder solid-state diffusion couples show a marked similarity to results found in this study. Palladium exhibited both parabolic and linear kinetics for solid- and liquid-state reactions, respectively. The activation energy for compound growth was $Q_s = 21.6$ kcal mol^{-1}, which is only slightly lower than the energy obtained in this study for platinum compound growth. The growth rates are not comparable, however, due to the much larger pre-exponential term in the growth equation for the palladium case. For example, a compound layer 8 μm thick would be predicted to form on palladium in

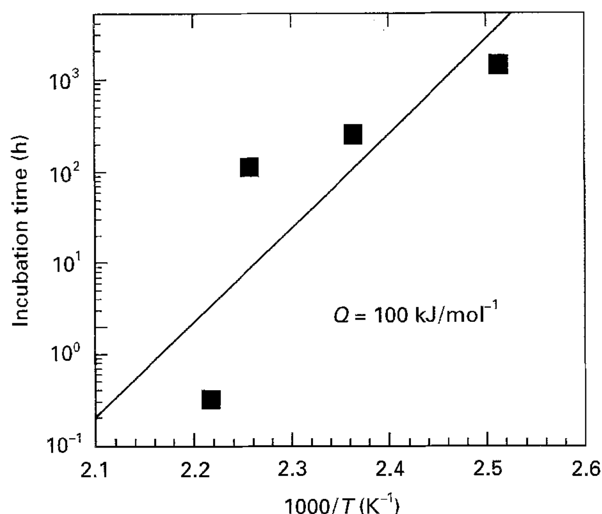


Figure 8 Arrhenius plot of incubation times for compound formation.

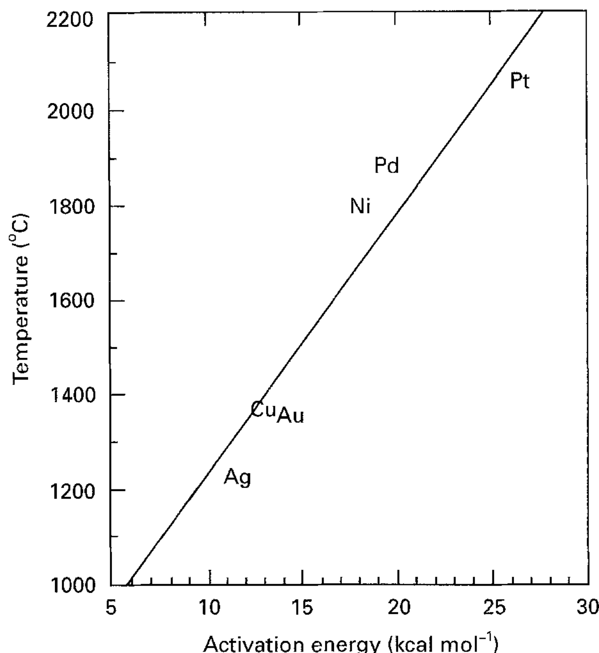


Figure 9 Activation energy for dissolution of several elements in solder as a function of their melting points.

about 10 min at 170 °C. To obtain a comparable layer thickness on platinum would require 400 h at this temperature, due in part to an apparent 200 h lag before the compound starts to grow. The extremely low compound growth rate indicates that platinum would make an excellent metallization material in contact with solder.

A striking feature of the growth data, which was alluded to above, is that the growth curves do not originate from the origin. This indicates that there is a delay time at temperature before parabolic growth develops. When such an incubation time was observed by Bader in his dissolution work, it was dismissed as being associated with the heating up of the wires, evaporation of the flux, etc. While these arguments may be plausible for incubation times on the order of seconds, they cannot account for the times observed in the present solid-state growth experiments. These incubation times, of the order of many hours, appear to be thermally activated. A crude Arrhenius plot shown in Fig. 8 yields an activation energy of 24 kcal mol^{-1} for this process. This energy is probably associated with the nucleation of $PtSn_4$ having a size sufficient to sustain further parabolic growth.

4.2. Dissolution experiments

Linear kinetics are the hallmark of a surface-controlled reaction step involving, in this case, the breaking of Pt–Pt bonds during dissolution. If the solder was not present, the heat of vaporization or the heat of fusion might, perhaps, approximate the energy required to remove atoms from the wire. The situation is vastly complicated by the presence of tin, which facilities the breaking of Pt–Pt bonds through formation of a $PtSn_4$ compound.

The activation energy value of 20.4 kcal mol^{-1} for dissolution (Fig. 7b) should be compared with energies of related processes. It is probable, but by no means certain, that platinum atom removal first occurs, followed by $PtSn_4$ formation, and then dispersal through the molten solder. The heat of vaporization for platinum is 127 kcal mol^{-1}, a value well above the dissolution energy measured. An extensive literature search did not turn up any values for the heat of formation, ΔH^0_{298}, of $PtSn_4$ for comparison. Very probably molten tin greatly facilitates atomic dissociation of platinum through, as yet, unidentified atomic interactions and mechanisms.

In closing, an interesting correlation is that activation energy for dissolution of various metals scales with the melting point. This is shown in Fig. 9, based on data reported by Bader [5], except for the value for platinum dissolution, which is taken from the present work. The correlation is not surprising in view of the fact that dissociation or bond breaking is involved in dissolution, and high melting points imply stronger bonds.

5. Conclusions

Results of this study show that the use of optical metallographic examination for diffusion studies of systems including solders is greatly complemented by SEM observations and EDX line scans. The uncertainties of locating phase boundaries are reduced if not eliminated with these analytical techniques.

Through the use of these methods it was found that solid-state intermetallic compound growth between platinum and 60 Sn–40 Pb solder followed parabolic kinetics even at temperatures close to the melting point of the solder. The intermetallic compound composition was identified as $PtSn_4$ by X-ray fluorescence analysis. Pt–Pb intermetallics were not observed in any test samples. These results suggest that platinum provides a metallization for soldering that is unlikely to present the intermetallic compound growth and reliability problems that have been encountered with gold and palladium.

Studies on the dissolution of platinum in molten solder showed that the loss of material was a three-stage process involving detachment of platinum, the formation of $PtSn_4$ and the subsequent spalling of this material and redistribution into the melt. The kinetics of dissolution are linear and proceed with an activation energy of 20.4 $kcal\,mol^{-1}$.

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