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PHASE DIAGRAMS OF (GOLD+BINARY SOLDER) TERNARY ALLOY SYSTEMS BY SMITH THERMAL ANALYSIS

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Abstract

Application of the Smith thermal analysis method [1] to the experimental determination of ternary alloy phase diagrams is illustrated by reference to a study of the Au–Pb–Bi system. This system, which is of interest in relation to soft-soldered interconnections in solid state device technology, exhibits a ternary eutectic and several transition peritectic reactions.

Keywords: alloy, Au–Pb–Bi system, phase diagrams, Smith thermal analysis

Introduction

On account of its unique combination of properties of high electrical and thermal conductivity, good corrosion resistance and excellent wetting features, gold is extensively used in solid state device technology to make contacts and connections [2]. A thin layer of gold applied to the electronic material enables joints to be made by eutectic bonding, by ultrasonic compression bonding or by soft-soldering. In soft-soldered interconnections to gold, a low melting binary or ternary alloy involving metals such as Pb, Sn, In, Bi is used. For multipass soldering operations a selection of different binary solders with different solidus–liquidus ranges is required to enable a sequence of stable joints to solid gold to be produced. For each individual solder a knowledge is required both of the melting range itself and the degree to which gold can dissolve in the liquid solder at temperature in order to assess the likely extent of the so-called 'scavenging' effect and to decide the Au-layer thickness required. Since to form a mechanically sound joint it is essential that the formation of brittle intermetallic phases in the soldered joint be avoided, it is also important to know which solid phases are formed either directly during solidification or subsequently as a re-

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sult of solid state transformation. Furthermore, the nature and amounts of the phases that exist at equilibrium in the soldered joints over the operating temperature range are important [3]. All of this information is contained in the Au–X–Y phase diagram, where *X–Y* is a binary solder system, and for this reason several of the relevant systems, e.g. Au–Pb–In [4, 5], Au–Pb–Sn [6, 7], Au–Pb–Bi [8], Au–Sn–Bi [9] have been studied in some detail. In the cases of Au–Pb–Sn, Au–Pb–Bi and Au–Sn–Bi the Smith thermal analysis technique was used because of the number and proximity of phase boundaries present in these systems. In this paper the basis of the Smith method [1] is explained, the experimental arrangement used in Smith studies is described and examples of phase boundary and invariant reaction experiments are discussed to illustrate the usefulness of this particular method in studying ternary alloy systems.

Smith thermal analysis

In the Smith method of thermal analysis [1], originally proposed in 1940 as a thermal analysis method permitting quantitative measurements of both specific and latent heats, the heating or cooling rate is not controlled directly. Smith suggested placing the specimen together with its measurement thermocouple inside a refractory container of low thermal conductivity. This in turn is placed inside a furnace the temperature of which is maintained a constant amount above or below the specimen temperature. This is achieved by means of a differential thermocouple which has one junction on the inside and one junction on the outside of the container; the emf from the differential couple is fed to the furnace controller. The controller adjusts the power input to the furnace to maintain the temperature difference across the wall of the container at some preset value. Under these conditions a constant temperature gradient is maintained across the container wall resulting in a constant rate of heat flow into or out from the specimen. It is this feature which distinguishes the Smith method from other thermal analysis techniques such as DTA or DSC.

Under the condition of constant heat flow the rate of change of sample temperature with time will in turn be determined by (i) the magnitude and sense of the rate of heat flow between the furnace and the sample and (ii) the thermal mass of the sample. For a single phase sample whose heat capacity is not strongly dependent on temperature, which is generally the case with most materials except in the vicinity of a second order change such as a magnetic or an order-disorder transformation, the rate of change of sample temperature with time on either heating or cooling will remain constant until a second phase with a different heat capacity appears. Thus, as the temperature of a single phase sample is changed and the boundary of a two phase field encountered, such as a liquidus temperature on cooling, this will be detected as a sharp change in the rate of change of sample temperature with time. This can be seen as follows for the case of a sample which is being heated or cooled in a temperature regime where heat flow occurs largely through conduction:

When a small quantity of heat q is supplied to or taken from n moles of sample of molar heat capacity C_p in time δt, there will be a change in temperature δT such that

$$q = nC_p\delta T$$

The amount of heat transferred in time δt will depend upon the temperature gradient $(T_2-T_1)/s$, the area A and the thermal conductivity k

$$q = Ak\left(\frac{T_2 - T_1}{s}\right)\delta t$$

where T_2 and T_1 are the temperatures of the furnace wall and sample respectively: s is the distance between junctions. Thus the rate of change of temperature with time is given by:

$$\frac{\delta T}{\delta t} = \frac{1}{C_p}\left(\frac{Ak}{n}\right)\left(\frac{T_2 - T_1}{s}\right)$$

In the Smith method the temperature difference (T_2-T_1) is maintained constant so that $(\delta T/\delta t)$ will remain constant provided C_p remains constant. When a second phase appears C_p will change and an abrupt change in $(\delta T/\delta t)$ will occur.

For a sample traversing a two phase region the effective C_p of the sample will be a weighted mean of the C_p's of the two phases with the amounts of the two phases being determined by the Lever Rule and the tieline end compositions. Thus, in general the rate of change of temperature with time will no longer be constant, but instead will vary smoothly with time in a manner determined by the shapes of the phase boundaries. As soon as the sample enters a three-phase field, for example in a ternary system, the appearance of the third phase will again be revealed by a sharp change in the plot of $(\delta T/\delta t)$ with time.

When a sample reaches an invariant reaction the temperature will remain constant until the reaction is complete. Thus with an appropriate heating or cooling rate the sample is always in a condition that is close to equilibrium. This enables invariant reactions that are close together in temperature to be studied by this method.

Experimental

The arrangement of experimental equipment is summarised in block diagram form in Figs 1(a) and 1(b). The low thermal mass furnaces required for Smith thermal analysis, which are not to our knowledge available commercially, were constructed in-house. The sample contains a single sheathed chromel-alumel thermocouple junction which serves both as the measurement couple and, in combination with the second junction in the furnace wall, as a differential couple for indicating and controlling the temperature difference between the sample and the furnace.

For measurement of the sample temperature, the signal from the hot junction is fed to an amplifier via a cold junction, then to an analogue to digital converter and to a microcomputer. After amplification the signal from the specimen thermocouple lies within the range from 0 to 1.2 V and the A to D converter converts this into a whole number between 0 and 4096 which means that it can resolve to approximately ±0.1°C. The computer program averages 3000 readings over a period of 15 s to give a mean value which is converted into a millivolt value using a third order polynomial expression obtained in separate calibration experiments. This calibration procedure involves determining the averaged A to D converter output numbers corresponding to the melting points of the following six metals Sb, Zn, Pb, Bi, Sn and In, each with a purity >99.9%. Frequent calibration runs are carried out to check that the temperature readings from the equipment reproduce each of the six pure metal melting points to within 0.5°C.

The rate of change of temperature is calculated from the temperature–time curve and averaged with the previous nine values so that only significant changes are shown. The specimen temperature, the averaged rate of change of temperature with time together with the plot of rate versus time, updated every 15 s, are displayed on the monitor and fed to a printer to provide a permanent record.

For controlling the temperature difference between the sample and the furnace a differential ±0.999 mV Controller type Micro 96 supplied by Newtronic Controls Ltd is used which monitors the temperature difference and adjusts the power input to the furnace element via a thyristor stack. In addition there is a set-point controller which can be used to homogenise the sample at any selected temperature prior to thermal analysis. In general, the sample is made by placing the weighed quantities of the pure elements in the silica sample tube, diameter 12 mm, and melting together under hydrogen to form approximately 1 cm^3 of single phase liquid. The sealed end of the thermocouple sheath, 3.0 mm o.d. silica tube, containing the chromel–alumel thermocouple, 0.2 mm diameter wire in twin bore alumina, is then immersed into this liquid alloy followed by rapid quenching into water at room temperature. Quenching the sample in this way results in a fine-grained microstructure which is essential to reduce diffusion distances to a minimum in order to promote rapid reaction rates.

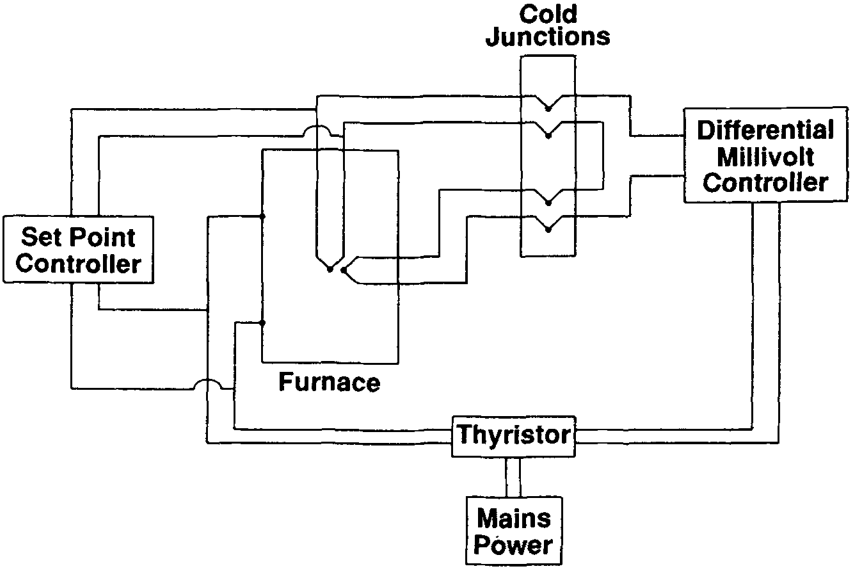

Fig. 1a Block diagram of control circuitry for Smith thermal analysis equipment

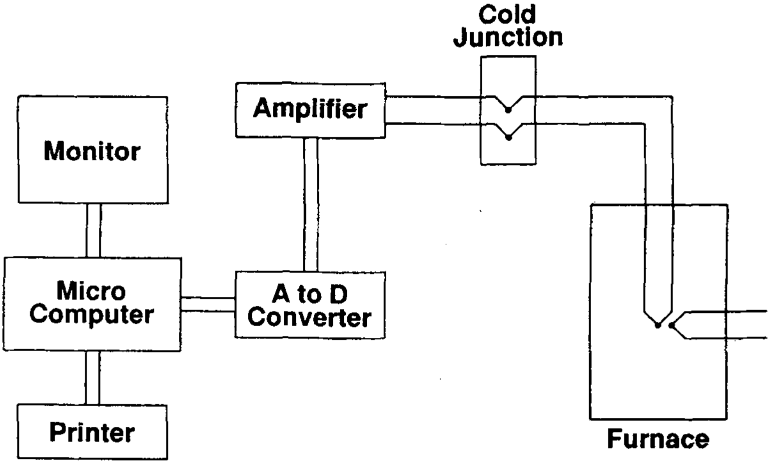

Fig. 1b Block diagram of specimen temperature measurement and data logging equipment

After melting and quenching the tube containing the sample and thermocouple sheath are placed in the Smith rig which in essence consists of a low thermal mass furnace which is capable of responding rapidly to the electronic controller. Experiments are conducted under flowing argon or high purity nitrogen and a bellows arrangement enables the specimen to be stirred by means of the measurement thermocouple sheath. The Smith rig also enables furnace-cooled samples to be obtained for metallographic study and phase identification and analysis. Both Nichrome wound furnaces operating with chrome–alumel thermocouples and Kanthal wound furnaces operating with Pt+Pt–13%Rh thermocouples have proved to be successful enabling phase equilibria in a variety of alloy systems to be studied in this laboratory [10–13].

Results and discussion

In this paper we illustrate the application of Smith thermal analysis to the study of ternary alloy phase equilibria by reference to the Au–Pb–Bi system in which the following ternary eutectic reaction has been shown to occur [8]:

$$\text{LIQUID} \rightleftharpoons \varepsilon + (\text{Bi}) + \text{Au(Pb,Bi)}_3$$

ε is the Pb-rich hcp secondary solid solution phase originating from the Pb–Bi binary system [14], (Bi) is bismuth-rich solid solution and $Au(Pb,Bi)_3$ is the $AuPb_3$ compound phase [15] in which some Bi substitution of Pb-atoms has occurred. At the eutectic temperature, the ($Liquid+\varepsilon+(Bi)+Au(Pb,Bi)_3$) four phase equilibrium is a horizontal triangular plane in temperature-composition space details of which are revealed experimentally by studying several vertical sections. Here we present some results for the $Pb_{0.5}Bi_{0.5}$ to Au vertical section which intersects the above ternary eutectic reaction plane.

Figure 2 shows results of a series of Smith thermal analysis heating runs for a sequence of ternary Au–Pb–Bi samples with a constant equiatomic ratio of Pb to Bi and with Au contents ranging from 2 to 18 atomic percent. The temperature range covered in these runs is approximately 100 to 130°C. For the composition range from 2 to 16 at% Au all of these plots of rate of change of temperature versus time have the same general shape. Initially the rate of change of temperature with time is constant with a value of about 1.2 $\text{deg}\cdot\text{min}^{-1}$, the rate then drops sharply to a value close to zero where it remains until it rises to a maximum and then either remains constant or decreases gradually and approximately linearly with time. The different portions of these curves correspond to the different phase fields and phase equilibria traversed by the various samples as heat is absorbed.

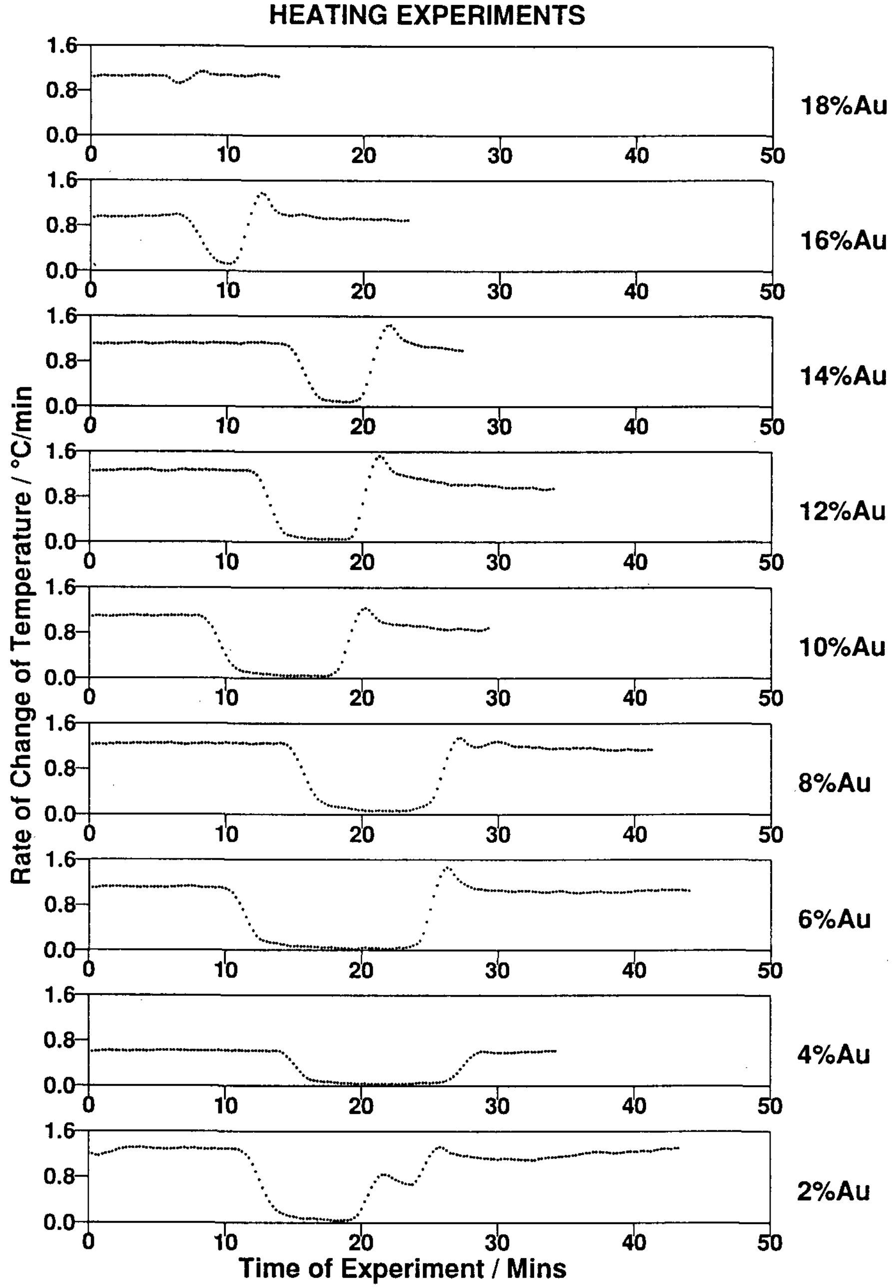

Fig. 2 Rate of change of temperature *vs*. time Smith thermal analysis heating traces for nine Au–Pb–Bi alloys on the $Pb_{0.5}Bi_{0.5}$ to Au section. Alloys with Au contents between 2 and 16 at% Au exhibit a ternary eutectic reaction

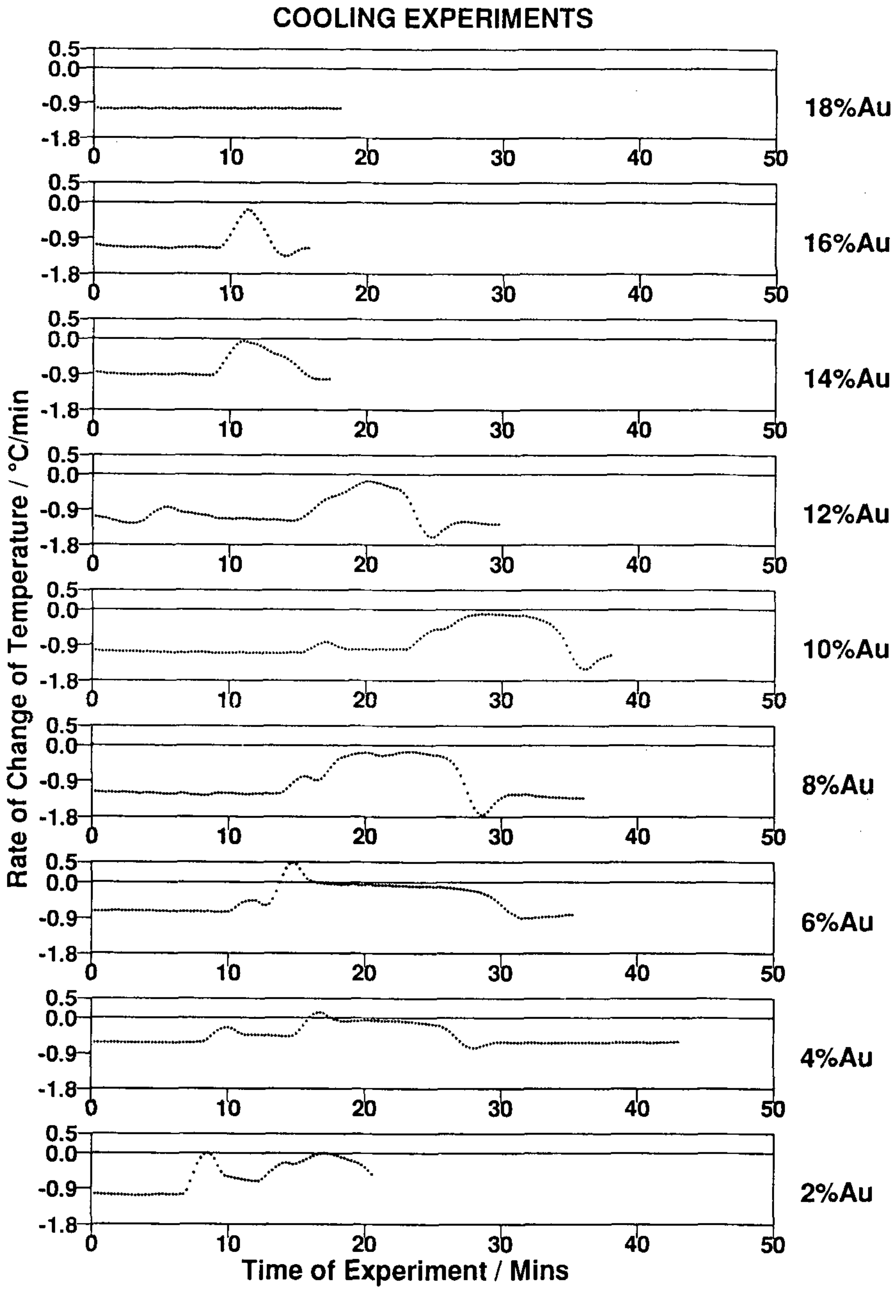

Fig. 3 Rate of change of temperature with time Smith thermal analysis traces for the same nine samples in Fig. 2 under cooling conditions

Initially the samples lie in the 3-phase (ε+(Bi)+Au(Pb,Bi)$_3$) phase field that lies below the invariant reaction plane. At each temperature the equilibrium phase compositions are the corners of the 3-phase triangle and, since these compositions are not strongly temperature dependent, for a given sample the relative amounts of the three phases remain constant resulting in a constant C_p and a constant rate of change of temperature $\delta T/\delta t$. When the sample arrives at the eutectic temperature liquid begins to appear giving a total of four phases, the system becomes invariant and at equilibrium its temperature must remain constant until one phase disappears. Thus the rate of change of temperature drops to zero, the sample absorbs heat isothermally and the eutectic reaction proceeds to completion. Eventually one of the solid phases will disappear and the temperature will begin to increase again. Depending upon the composition of the sample, the system will now enter the (liquid+ε+(Bi)), (liquid+ε+Au(Pb,Bi)$_3$) or the (liquid+(Bi)+Au(Pb,Bi)$_3$) 3-phase field. A sample having the exact composition of the eutectic liquid would go directly into the single liquid phase field. The amount of liquid formed in a sample at the eutectic temperature depends on the sample composition, the nearer the sample composition lies to the eutectic liquid composition the higher the liquid volume fraction formed and the stronger the reaction. This is evident in the sequence shown in Fig. 2 where the strength of the eutectic reaction, as evidenced by the time at which the temperature remains constant, initially increases from 2–4 at% Au, reaches a maximum at 4–6 at% Au and then becomes progressively weaker with increasing Au-contents beyond 8 at% until at 18 at% Au the eutectic reaction is not observed. This composition therefore lies outside the 4-phase triangle.

Following the eutectic reaction there is a peak in the $\delta T/\delta t$ *vs.* time curve which is thought to arise as follows: liquid formed by the eutectic reaction is heated slightly above the invariant temperature due to the finite rate at which the eutectic reaction can occur whereas the solid phases have a temperature close to the invariant reaction temperature itself. As soon as the last traces of the third solid phase disappear the system is no longer invariant and the sample temperature can even out by a transfer of heat from the liquid phase to the two remaining solid phases. The recorded temperature being a mean of the solid and liquid temperatures will therefore increase giving a maximum in the $\delta T/\delta t$ *vs.* time curve. Beyond this maximum the rate of change of temperature will depend upon where the sample composition lies in relation to that of the eutectic liquid. The nearer the sample composition to the eutectic point the lower the rate of change of temperature will be. Away from eutectic point further melting has to occur above the eutectic temperature thereby changing the weighted C_p value of the sample which in turn results in a $\delta T/\delta t$ which changes with time. All of these features can be seen in Fig. 2. Additional peaks beyond the eutectic reaction can be seen in some of the traces in Fig. 2 e.g. in those for the 2 and 8 at% Au samples. These are the thermal arrests for the boundary between the 3-phase and the 2-phase regions above the eutectic, i.e. the curves of secondary separation.

Figure 3 gives the Smith thermal analysis cooling runs for the same samples and the same temperature range discussed above. In each case it is seen that a point is reached where the rate of change of temperature with time changes

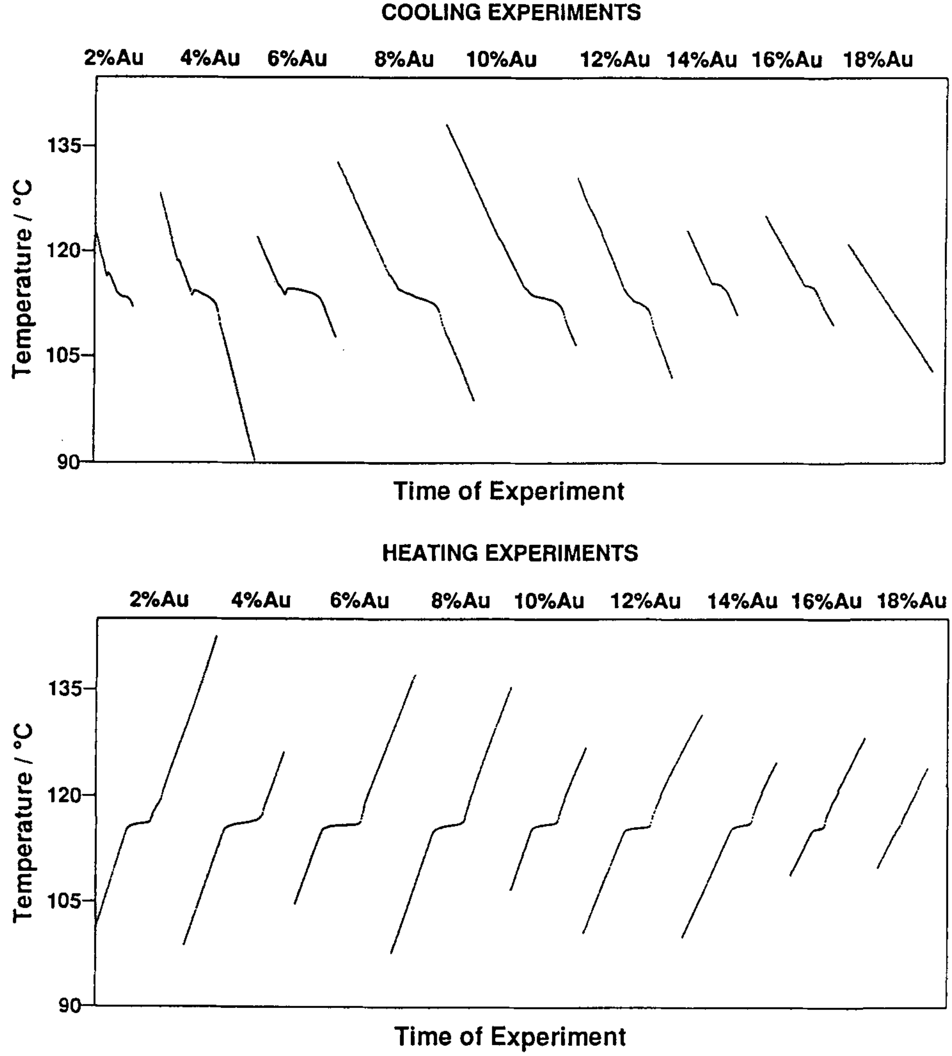

Fig. 4 Temperature *vs.* time curves for the Smith thermal analysis experiments given in Figs 2 and 3; upper curves are the cooling runs, lower curves are the heating runs

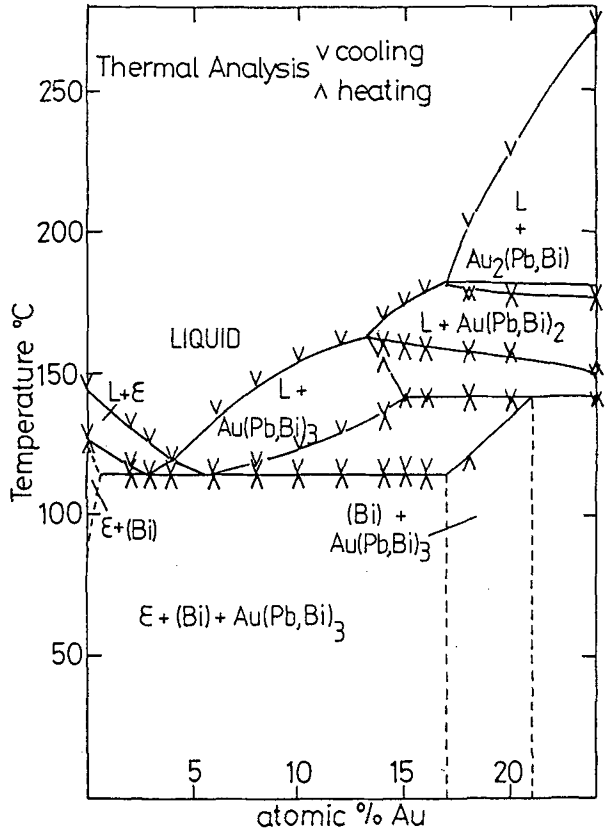

Fig. 5 The $Pb_{0.5}Bi_{0.5}$ to 24 at% Au vertical section in the Au–Pb–Bi system determined by Smith thermal analysis showing the ternary eutectic reaction at 115.2°C and the transition peritectic reaction at 142°C

sharply from the steady state value and then approaches zero. In the absence of any supercooling as evident from the temperature-time curve it is this point which is taken as the onset temperature for the invariant reaction. For the samples with compositions close to the eutectic point, i.e. 4 and 6 at% Au, where the phase fraction of liquid is at its highest on this vertical section supercooling occurs below the invariant temperature. When the reaction does start a rapid release of enthalpy occurs which causes the sample to be reheated to the invariant reaction temperature. In these cases immediately following the supercooling stage the rate of change of temperature becomes positive and then becomes zero (or close to zero) at the start of an isothermal stage. In these cases the invariant reaction temperature is taken as the maximum temperature reached following supercooling. During the eutectic reaction the rate remains close to zero and then drops sharply to a minimum value before assuming a constant value for the solid alloy. Additional peaks are again evident corresponding to the other phase boundaries. Again in the 18 at% Au sample there is no evidence of a eutectic reaction.

For comparison with the above results Fig. 4 gives the measured temperature-time heating and cooling curves for the same experiments. The onset of reaction is clearly evident together with the increase in temperature in the cooling

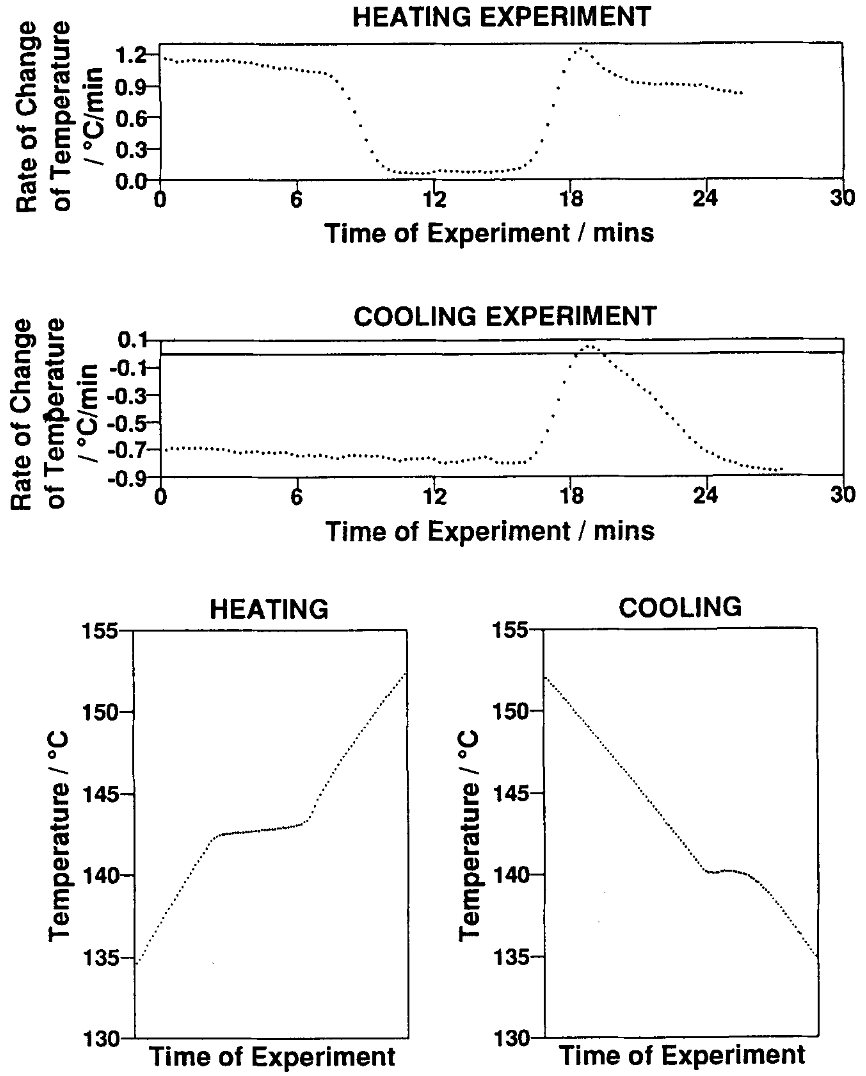

Fig. 6 Transition peritectic reaction: upper diagrams are Smith heating and cooling traces; lower diagrams are the corresponding temperature–time plots

runs. The start temperature of the reaction on heating equals the maximum temperature reached during reaction in the cooling experiments within experimental error.

Figure 5 shows the partial $Pb_{0.5}Bi_{0.5}$ to Au vertical section from the binary Pb–Bi edge to 24 at% Au. Included with the results of the above experiments are the results of other experiments carried out to define the phase boundaries and phase reactions. It is seen that the ternary eutectic reaction lies at 115°C. For this and other sections where the present eutectic reaction occurs, a total of twenty-six individual heating runs were performed which gave 115.2°C for the eutectic reaction with a standard deviation of 0.7 degrees. This temperature is 11.3 degrees below the eutectic reaction in the Pb–Bi binary system. Also in this section can be seen a transition peritectic reaction at 142°C corresponding to the following four phase equilibrium:

$$\text{LIQUID} + \text{Au(Pb,Bi)}_2 \rightleftharpoons \text{Au(Pb,Bi)}_3 + \text{(Bi)}$$

For comparison purposes the heating and cooling Smith thermal analysis runs for the 18 at% Au sample undergoing the transition peritectic reaction are given in Fig. 6. It can be seen that the $\delta T/\delta t$ *vs.* temperature plot on heating is similar to those above for the ternary eutectic reaction. However the plot for the cooling runs differs from the corresponding ones for the eutectic reaction in that the rate increases to a positive value following an initial undercooling and then drops steadily without a pronounced minimum value. This is also seen in the lower temperature versus time curves where the maximum temperature on cooling lies below the start temperature on heating. This is attributed to the self-limiting nature of peritectic reactions where the reaction product formed at the liquid-solid interface effectively inhibits reaction thereby preventing a four phase equilibrium being established at the invariant temperature.

Conclusions

1. The Smith thermal analysis method is well suited to the experimental determination of ternary alloy phase diagrams particularly those which contain many phase boundaries and invariant reactions.

2. In the Smith method the sample is maintained in a condition close to equilibrium thereby enabling invariant reactions to go to completion isothermally in both heating and cooling experiments. It is this feature that in the present work has enabled phase boundary temperatures that lie close to the invariant reaction to be resolved and measured.

3. In the study of ternary eutectic reactions by Smith thermal analysis the invariant temperature should be taken as the observed start temperature on heat-

ing and as the maximum temperature after the initial supercooling effect in a cooling run.

4. For transition peritectic reactions the rate of change of temperature *vs.* time curves for heating runs are similar to those for ternary eutectic reactions whereas for cooling runs there are differences which is ascribed to the self-limiting nature of these reactions.

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Zusammenfassung — Anhand einer Untersuchung des Systemes Au-Pb-Bi wurde die Anwendung der thermoanalytischen Methode von Smith [1] zur experimentellen Bestimmung von ternären Legierungsphasendiagrammen gezeigt. Dieses System mit Bedeutung für weichgelötete Verbindungen in der Technologie der Festkörperbauelemente weist ein ternäres Eutektikum und einige peritektische Umwandlungsreaktionen auf.