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Calculation of Phase Equilibria in Candidate Solder Alloys

Dedicated to Prof. Dr. Dr. h.c. mult. Günter Petzow on the occasion of his 75th birthday

Abstract

New solder alloys are being developed for electronic assemblies as replacements for traditional Pb-containing solder materials as a result of international pressure to remove Pb from the waste stream. In the transition period from Pb-containing to Pb-free solder alloys, component leads and copper interconnections on circuit board will continue to be pre-tinned with a Pb-containing solder to improve solderability. Phase equilibria information is needed for the evaluation of candidate Pb-free solder alloys in terms of their melting behavior and of the possible effects of Pb-contamination on manufacturing and reliability. The CALPHAD method of phase equilibria calculation using thermodynamic descriptions from databases provides a powerful tool for obtaining such information. The reliability of the calculation, however, depends on the quality of the thermodynamic descriptions of the individual phases. Criteria for the evaluation of these descriptions and the available thermodynamic databases are discussed. The effect of Pb-contamination on four solder alloys is analyzed.

1 Introduction

In the last five years the microelectronics industry has been moving away from Pb-containing solder alloys for two reasons. First, there is a growing interest worldwide in removing toxic elements, including Pb, from the solid waste stream for electronic equipment. Second, the automotive industry is developing solders that withstand higher service temperatures characteristic of under-the-hood applications. For these purposes it is necessary to evaluate the properties of candidate solders related to manufacturing and reliability, such as freezing

range (liquidus, solidus), effects from possible contamination from other solder materials and reactions with various substrates, and solderability. Most Pb-free solders are Sn-based alloys with additions of low melting metals such as Bi, Sb and In or metals forming a eutectic reaction with (Sn)*, such as Ag and Cu. Since common substrate materials consist of Cu, Cu coated or plated with Sn-Pb or Sn-Bi solders, Ni-Sn, Ni-Au and Ni-Pd, the systems containing these elements in combination with the solder elements also need to be evaluated.

Although extensive research has been carried out on the phase diagrams of most binary Sn-systems, data may be not available for every higher-order Sn-based system. However, when the binary sub-systems are known, thermodynamic calculation provides an extremely useful tool for obtaining quantitative information about the higher-order (ternary, quaternary, *etc.*) systems. For a ternary system, for example, thermodynamic models consistent with the experimental binary data are first obtained, then a standard thermodynamic extrapolation method is used to calculate the ternary system. This approach is part of the CALPHAD method [1,2]. From the calculated phase diagram, the melting temperature range for solder, the solidification path, as well as the susceptibility to intermetallic formation with various substrates, can be estimated. The CALPHAD method also allows the calculation of equilibria for compositions and temperatures where data are not available, as well as calculation of metastable equilibria.

Thermodynamic calculation also provides data for the analysis of other alloy properties. Analysis

* The elemental symbol in parenthesis is used to distinguish the disordered solid solution based on this element from the pure element.

of multi-component diffusion requires that tie-line information, *i.e.*, the compositions of two phases in equilibrium, be available [3]. Tie-line data are rarely measured but can be easily obtained from the calculated phase equilibrium.

The wetting behavior of a molten solder is an important property which partially depends on the surface tension and viscosity of the liquid phase. Lee and Lee [4] used the correlation between the partial excess Gibbs energies and the surface tension to calculate the surface tension of binary solder liquids. The partial excess Gibbs energies are quantities that are readily available from the thermodynamic calculation. The correlation between the thermodynamic properties of the liquid phase and surface tension, as well as the viscosity, was also used by Ohnuma *et al.* [5].

The subject of this paper is to give criteria for the evaluation of the thermodynamic assessments of binary and ternary systems relevant to solder alloys and to give a survey of the available thermodynamic databases. Examples of the utilization of information from the phase diagrams, as well as the thermodynamic calculation, for the evaluation the effect of Pb-contamination on the freezing ranges of solder alloys will be presented.

2 The Calculation of Phase Equilibria

2.1 Choice of Models

The CALPHAD method [1,2] employs a variety of models for the descriptions of the various phases. The choice of model used for the description of each phase is important since it determines the compatibility of all possible binary systems in which phases with the same or similar crystal structures occur. The crystallographic relationship between two phases of different binary systems is sometimes obscured by the fact that they have different stoichiometries. For example, the high- and low-temperature η and η' phases of the Cu-In and the Cu-Sn systems occur at 33-38 % In and 43.5-45 % Sn (atomic fraction), respectively, and are, therefore, associated with different stoichiometries, *i.e.*, Cu_2In and Cu_5Sn_6 . Despite their apparently different stoichiometries, the need for the same model for the two phases is necessary for the Cu-In-Sn system since the high-temperature phase shows a continuous ternary solid solution [6]. The crystal structure of both of these phases belongs to the $\text{B8}_1/\text{B8}_2$ ($\text{NiAs}/\text{Ni}_2\text{In}$) structure type family and can be successfully described with the same model description [7]. Another family of related structures are the D8_2

and D8_3 structures (Cu_5Zn_8 and Cu_9Al_4 , respectively). These two phases form continuous ternary solutions in the Al-Cu-Zn system [8] as well as in the Cu-Ga-Zn (Cu_5Zn_8 and Cu_9Ga_4) system [9]. The modeling of these two structures with the sublattice model would require a complex description with 4 sublattices [10]. In order to simplify the description of this phase, Liang and Chang [11] modeled it as a disordered solution. It is not uncommon to make such simplifications in the thermodynamic assessment of a complex system. Other common simplifications are: to describe a solid phase with a narrow homogeneity range as a stoichiometric compound; to omit a phase which is only stable in a narrow temperature interval and assess the metastable diagram instead; and to treat two or more phases with related crystal structures as one phase, thus ignoring the transformation between them. These simplifications are acceptable as long as care is taken not to compromise general and important features of the system.

2.2 Selection Criteria for Assessments

It is desirable to utilize as many of the existing binary assessments as possible in order to allow rapid assessment of higher-component systems. Therefore, it is necessary to select a set of binary assessments as a basis for a database for solder systems. An obvious requirement is that calculated phase equilibria data reproduce the experimental data within the limits of the experimental accuracy. In the case of solder alloy systems, where the invariant temperatures are known within a few tenths of degrees, it is paramount that these temperatures are reproduced within this limit. However, the true test of the quality of the thermodynamic description is the extrapolation to a ternary system. One example where the quality of the thermodynamic description was found to be insufficient is the Sn-rich part of the Sn-Ag-Cu system. In this case, the calculation does not reproduce the ternary eutectic within the limits of the experimental error [12]. Moon *et al.* [12] found that the description of the liquid + Ag_3Sn and liquid + Cu_6Sn_5 equilibria in the binary Ag-Sn and Cu-Sn systems is in need of further refinement in order to obtain better agreement with the ternary system. However, the available experimental data for the Sn-rich part of these two binary systems scatter noticeably. Therefore, the further refinement of these description must either utilize ternary data or improved new experimental data of the binary systems.

Extrapolation to higher-component systems is one reason why a large number of terms in the

concentration dependence of a solution phase is undesirable. In an extrapolation, a large number of terms can result in a "bumpy" Gibbs energy function, creating unlikely shapes in phase boundaries. Alternatively, a phase may appear to be stable in a composition/temperature region of the system where it is not observed in the equilibrium diagram. In order to combine ternary assessments for the extrapolation to a higher-component system, all of the ternary assessments must be based on the same binary descriptions. The substitution of one binary description by another in a ternary assessment will require a reevaluation of the ternary description in most cases.

2.3 Advantages of Calculated Phase Diagrams

If all of the above criteria are fulfilled, the phase diagram that is obtained from a ternary assessment can actually be more accurate than the one from a critical evaluation, as is the case for the Ag-Cu-Pb system. The calculated liquidus surface [13] differs from the one proposed in evaluations [8,14,15] where the liquidus surface was based on the early interpretation of the results of Friedrich and Leroux [16]. Jänecke [14] based his evaluation on the then accepted Cu-Pb phase diagram for which the miscibility gap in the binary liquid phase was greatly overestimated and, accordingly, resulted in an overestimation of the ternary miscibility gap in the liquid phase. This evaluation was later accepted in the evaluations by Chang *et al.* [8] and Hayes [15]. The calculation of Hayes *et al.* [13] is based on a revised Cu-Pb system with a much less pronounced liquid miscibility gap and the original data of Friedrich and Leroux [16] as well as thermodynamic data. Since both phase diagram data and thermodynamic quantities are generated from the same thermodynamic description and are, therefore, consistent, the calculated liquidus surface is more realistic than the critically evaluated liquidus data.

3 Available Phase Equilibria Information for Candidate Solders

3.1 Binary Systems

Several of the phase diagrams of binary solder systems are fairly simple. However, almost two thirds of the binary systems have at least one intermetallic compound. A summary of binary intermetallic phases and their structures for the most common elements in solder alloys is given in

Table 1. For the binary systems which do not contain intermetallic compounds, there exist at most three phases (the low-temperature modification of Sn, α Sn, can be neglected for solder applications). The simplest of these systems is the Bi-Sb system where both the liquid and the solid phases form continuous solid solutions. Many of these simple systems, *e.g.*, Ag-Bi, Ag-Cu, Ag-Pb, Bi-Cu, Bi-Sn, Ga-In, Ga-Sn, Ga-Zn, In-Zn, Pb-Sb, Pb-Sn and Sn-Zn, are eutectic. In other systems, such as Ag-Cu, Ag-Pb and Cu-Pb, the solid two-phase equilibria are the result of a miscibility gap in the fcc phase. Other systems form miscibility gaps in the liquid phase, including Bi-Ga, Bi-Zn, Cu-Pb, Ga-Pb and Pb-Zn. Thermodynamic assessments with SGTE compatible lattice stabilities [17] for the description of the pure elements are available for most of these systems.

Many of the binary systems relevant to solders form intermetallic compounds, making their description fairly complex since several phases with ordered structures exist. In a few systems, one or two of the intermetallic phases have a disordered site occupation in their crystal structure, *e.g.*, Bi-Pb, Ag-Sn, In-Pb and In-Sn. These disordered phases frequently show significant homogeneity ranges. Since the crystal structures of these phases can be the same as disordered elemental structures, the same model descriptions as for the corresponding elemental phases should be used. Other systems, such as Ga-Sb and In-Sb, have only one compound with a very narrow homogeneity range.

3.2 Ternary and Higher-Component Systems

Including the most common 8 elements for solder alloys, Ag, Bi, Cu, In, Pb, Sb, Sn and Zn, results in consideration of 56 ternary systems that are relevant to solders. Since the experimental determination of a ternary system is extremely time consuming, a sufficient number of experiments has been carried out for only about a quarter of these systems to establish their phase diagrams reasonably well. Some experimental data are available establishing a partial phase diagram for almost half of the remaining systems. No experimental information is available for the remaining quarter of the systems. Critical evaluations of the experimental data are available for ternary Ag-, Al- and Au-systems [18] and Cu-systems [8]. Villars *et al.* [19] compiled a summary of the available experimental phase diagram data for ternary systems.

If thermodynamic descriptions of all of the constituent binary systems are available, it is possible to estimate a phase diagram of a higher-component system from the extrapolation of the binary systems. The quality of the extrapolation to a ternary system from the descriptions of the three binary systems depends not only on the accuracy of the calculation of each binary system, but also on the magnitude of possible ternary interactions and the occurrence of ternary intermetallic compounds. The probable magnitude of these ternary interactions can be estimated from the properties of the binary systems. In most cases the excess Gibbs energies of the solution phases in the binary systems relevant to solder alloys are relatively small in magnitude, indicating that ternary interactions are probably not significant. This was demonstrated by Kattner and Boettinger for the case of the Cu-Pb-Sn system [20]. Many of the binary systems show no tendency to form intermetallic compounds, suggesting that the formation of ternary intermetallic compounds in higher-component systems based on these systems is also unlikely. In fact, only two ternary intermetallic compounds have so far been reported for those of the 56 ternary systems which have been experimentally measured. In the Cu-In-Sn system [6] the structure of the $\text{Cu}_{11}\text{In}_2\text{Sn}$ phase is an ordered bcc structure and can, therefore, be related to binary intermetallic phases of the Cu-In and Cu-Sn systems. In the Sb-Sn-Zn system [21] the structural relation of the Sb_2SnZn phase to the binary phases is not known.

3.3 Available Thermodynamic Databases

The efforts in the development of thermodynamic descriptions for systems that are relevant to solders have resulted in several thermodynamic databases that are either available in the public domain [4,22] or are commercial† [5]. These databases are usually built from the assessed descriptions of all binary constituents systems but not necessarily all ternary systems. The database described by Lee and Lee [4] includes seven elements (Sn, Ag, Bi, Cu, In, Sb, Zn) and the assessments of all constituent binary systems and selected ternary systems. The database described by Ohnuma *et al.* [5] includes assessed descriptions for all binary and ternary systems including elements Sn, Ag, Bi, Cu, Pb, Sb, Zn and selected systems containing In. The

† Commercial products are referenced for completeness. Such identification does not imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply that these products are necessarily the best available for the purpose.

description of the Sn-Pb systems includes also the pressure dependence of the Gibbs energy of the phases. Another database under development [22] currently includes assessed descriptions of all binary systems and selected ternary systems for the elements Sn, Ag, Bi, Cu, Pb.

4 Freezing Temperature Ranges

4.1 Equilibrium Solidification

A basic requirement for a candidate solder alloy to replace a Pb-containing solder is to have a specific freezing range, the temperature range over which both solid and liquid co-exist; this freezing range is dictated by the application. To replace the Pb-Sn eutectic alloy, the ideal solder alloy would be eutectic or near-eutectic, with a liquidus temperature low enough to avoid damaging components and a solidus temperature high enough to maintain joint reliability during thermomechanical fatigue.

One limiting case for describing solidification behavior is solidification obeying the lever rule (thermodynamic equilibrium). For equilibrium solidification (lever rule) it is assumed that at each temperature during cooling, complete diffusion occurs in the solid as well as in the liquid and, therefore, all phases are in thermodynamic equilibrium at each temperature. The equilibrium freezing range of a binary alloy can be easily read from a phase diagram or from the isopleths for higher-component systems. However, isopleths provide information only for one section through the multi-component phase diagram and, since the tie-lines are usually not in the plane of the isopleth, there is no information on phase compositions and amounts. In the case of ternary systems this information can be obtained from simultaneously examining the liquidus and solidus projections of the ternary system. These diagrams do not provide information about the onset of the formation of a second solid phase. Thermodynamic calculations, however, can be used to calculate the equilibrium solidification path for individual alloys and to generate tables with the desired numerical quantities, such as tie-line data, phase amounts or enthalpy content.

4.2 Non-Equilibrium Solidification

Even if the phase diagram shows that a specific alloy has the desired freezing range, it is possible, and quite likely for non-eutectic freezing, that a larger freezing range is observed in experiments. This is the case when non-equilibrium solidification occurs. Since the degree

to which non-equilibrium solidification occurs is determined by kinetic factors, it is difficult to predict. The limiting case describing this solidification behavior is the Scheil path, where diffusion in the solid is forbidden. Thermodynamic equilibrium exists only as local equilibrium at the liquid/solid interface. This produces the worst case of microsegregation with the lowest final freezing temperature. Since the composition of the remaining liquid phase varies according to the tie-lines it is usually not possible to obtain the Scheil path from an isopleth. However, the Scheil path can be easily obtained from thermodynamic calculation. Although modeling of real solidification behavior requires the incorporation of a kinetic analysis of microsegregation and back diffusion, the predictions of the Scheil model are close to reality for many alloys for the time scales found in soldering.

4.3 Contamination of Pb-free Solders

The use of a pre-tinning alloy for component leads and copper circuit board interconnects with components and pads with different composition than that used for the solder may result in degraded properties of the solder joints. For example, when Pb-free solder alloys are contaminated by Pb from the pre-tinned layer, these alloys may form a low melting higher-component eutectic. This case was studied in detail for Pb-contaminated Sn-Bi solders by Moon *et al.* [23] using experimental methods in conjunction with calculations of the equilibrium phase diagram and Scheil solidification. They found that a small amount of contamination by Pb results in the formation of this low melting eutectic at 98°C. The predictions from the Scheil path calculations were in accord with their experimental observations.

Since the freezing ranges of other Pb-free solder alloys may be similarly susceptible to Pb-contamination, the freezing behavior of four solder alloys was studied from the calculation of the lever rule and Scheil freezing path of the original solder alloy and the contaminated solder. Moon *et al.* estimated a Pb-concentration of 6 % (mass fraction) in the solder from contamination by the component lead and board pre-tinning. The original solder compositions and those resulting from contamination are listed in Table 2. The calculations were carried out using the NIST solder database [22], the Thermo-Calc software package [24] and the Scheil and Lever programs [25].

Fig. 1 shows the calculated isopleths from the original solder composition to the composition of the contaminant for sections through the multi-component solder system. The phases that are formed during equilibrium solidification can be obtained from these sections. The diagrams show also that Pb-contamination for solders without Bi results in the formation of eutectic equilibria with slightly lower temperatures than the binary Sn-Pb eutectic (Ag-Pb-Sn: 177 °C, Ag-Cu-Pb-Sn: 176 °C). However, as previously mentioned, phase compositions, *i.e.*, tie-line information, phase fractions as well as information about Scheil path solidification, cannot be obtained from these diagrams.

Lever rule and Scheil path calculations were performed for each of the alloy compositions listed in Table 2. The results of these calculations are summarized in Fig. 2 and Tables 3 and 4. The compositions of the Bi-free solders are identical or close to the compositions of the Sn-rich eutectics of the Ag-Sn and Ag-Cu-Sn systems. Thus, the freezing ranges of these alloys are small and essentially identical for lever rule and Scheil solidification. Pb-contamination of these alloys results for both alloys in the formation of higher-component eutectics where solid (Pb) is formed. Since freezing of the Pb-contaminated alloys ends for both lever rule and Scheil solidification with the eutectic reaction the solidification behaviors are similar. The effect of Pb-contamination on the solders with Bi is different. The combination of Sn, Bi and Pb results in the formation of low melting eutectics ($T = 98\text{ °C}$) that are very close to the Bi-Pb-Sn ternary system and do not extend to compositions of the isopleths (Fig. 1). However, depending on the Pb-concentration, the liquid phase is stable at fairly low temperatures. Since the lever rule solidification is not terminated by eutectic freezing it can be expected that Scheil solidification will result in lower final freezing temperatures which can be as low as the low-melting eutectics of these systems. Eutectic final freezing is observed for the Scheil path for the Sn-2.9Ag-4Bi-6Pb alloy but not for the Sn-2.8Ag-0.8Cu-2.8Bi-6Pb alloy and is a consequence of the lower Bi concentration in that alloy. This behavior is in accord with the observations by Moon *et al.* [23].

In a recent summary of fatigue resistant, high temperature solders Gayle[26] gave a target storage and operating temperature of -55 °C to +160 °C and noted that the Bi concentration for these alloys must be kept below 3.5 % to avoid problems with low melting eutectic in case of Pb-

contamination. Although the present results confirm that the formation of the low melting eutectic does not occur during Scheil solidification of an alloy with a lower Bi-concentration after Pb-contamination, the liquid phase is a stable phase at temperatures below 160 °C. Bi containing solders should, therefore, completely be avoided for these applications if there is the possibility of Pb-contamination.

Contamination of solders is not a problem associated only with Pb but will always pose a possible problem when the constituent elements from the solder and the pre-tinning material are different. For example, pre-tinning with a Bi-containing alloy could cause the formation of the low melting eutectics in which solid (Sn) and (Bi) form. However, current practices use pre-tinning alloys with fairly low Bi-concentrations compared to 37 % Pb of the Sn-Pb alloy, therefore, the effect from the contamination can be expected to be much less pronounced than found for Pb-containing pre-tinning alloys.

5 Conclusion

The calculation of phase diagrams and properties from thermodynamic databases is a powerful tool for the development of new solders needed worldwide for Pb-free electronic assembly. A wide range of potential alloys can be relatively rapidly evaluated and potential problems with non-equilibrium freezing or contamination with other elements can be analyzed provided adequate thermodynamic databases exist. Thermodynamic calculations further provide data that are needed for the prediction of other solder properties such as surface tension and viscosity of the liquid phase.

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Table 1: Crystal Structures of the Solid Phases in Binary Solder Systems

System	disordered phases						ordered phases			
	A1: fcc	A2: bcc	A3: hcp	A5: β Sn	A6: In	A7: α As	fcc	bcc	hcp	other
Ag-Bi	(Ag)					(Bi)				
Ag-Cu	(Ag), (Cu)									
Ag-In	(Ag)	β	ζ		(In)		L1 ₂ : Ag ₃ In	D8 ₃ : Ag ₂ In		C16: AgIn ₂ ?: α'
Ag-Pb	(Ag), (Pb)									
Ag-Sb	(Ag)		ζ			(Sb)				L6 ₀ : Ag ₃ Sb
Ag-Sn	(Ag)		ζ	(Sn)						D0 ₃ : Ag ₃ Sn ?: ϵ'
Ag-Zn	(Ag)	β	ϵ , (Zn)					D8 ₂ : Ag ₅ Zn ₈	B ₆ : ζ AgZn	
Bi-Cu	(Cu)					(Bi)				
Bi-In					(In), ϵ ?	(Bi)			B8 ₂ : BiIn ₂	B10: BiIn D8 ₁ : Bi ₃ In ₅
Bi-Pb	(Pb)		ϵ			(Bi)				
Bi-Sb						(Bi,Sb)				
Bi-Sn				(Sn)		(Bi)				
Bi-Zn			(Zn)			(Bi)				
Cu-In	(Cu)	β			(In)			InMn ₃ : γ	B8 ₁ : Cu ₂ In.h B8 ₂ : Cu ₂ In.l ?	Cu ₇ In ₃ : Cu ₇ In ₃ AlCu: Cu ₁₁ In ₉
Cu-Pb	(Cu), (Pb)									
Cu-Sb	(Cu)		γ			(Sb)		D0 ₃ : β	?: δ	D0 ₃ : Cu ₃ Sb Cu ₁₀ Sb ₃ : Cu ₁₀ Sb ₃ C38: Cu ₃ Sb
Cu-Sn	(Cu)	β		(Sn)				D0 ₃ : γ Cu ₄₁ Sn ₁₁ : Cu ₄₁ Sn ₁₁	B8 ₁ : Cu ₆ Sn ₅ .h B8 ₂ : Cu ₆ Sn ₅ .l ? Cu ₁₀ Sn ₃ : Cu ₁₀ Sn ₃ Cu ₃ Sn: Cu ₃ Sn	
Cu-Zn	(Cu)	β	ϵ , (Zn)					B2: β' D8 ₂ : Cu ₅ Zn ₈ ?: δ		
In-Pb	(Pb)				(In), α					
In-Sb					(In)	(Sb)	B3: InSb			
In-Sn				(Sn)	(In), β					hex: γ
In-Zn			(Zn)		(In)					
Pb-Sb	(Pb)					(Sb)				
Pb-Sn	(Pb)			(Sn)						
Pb-Zn	(Pb)		(Zn)							
Sb-Sn				(Sn)		(Sb)	B1: β			?: Sb ₂ Sn ₃
Sb-Zn			(Zn)			(Sb)				B _c : SbSn ?: γ , ϵ , δ , ζ , η
Sn-Zn			(Zn)	(Sn)						

Table 2: Modified solder compositions as a result from contamination with 16.2 % of Sn - 37 % Pb solder. (Compositions are in % of mass fraction)

Original Solder Composition	Contaminated Solder Composition
Sn - 3.5 % Ag	Sn - 2.9 % Ag - 6 % Pb
Sn - 4 % Ag - 1 % Cu	Sn - 3.4 % Ag - 0.8 % Cu - 6 % Pb
Sn - 3.5 % Ag - 4.8 % Bi	Sn - 2.9 % Ag - 4 % Bi - 6 % Pb
Sn - 3.4 % Ag - 1 % Cu - 3.3 % Bi	Sn - 2.8 % Ag - 0.8 % Cu - 2.8 % Bi - 6 % Pb

Table 3: Liquidus, final freezing temperatures, and mass fraction of low-melting eutectic from the lever rule and Scheil calculations without and with Pb-contamination.

	Sn-3.5Ag		Sn-4Ag-1Cu		Sn-3.5Ag-4.8Bi		Sn-3.4Ag-1Cu-3.3Bi	
	T (°C)	f _e	T (°C)	f _e	T (°C)	f _e	T (°C)	f _e
Solder								
Lever	221	-	225-215	-	215-201	-	233-204	-
Scheil	221	-	225-215	-	215-137	0.03	233-137	0.02
Contaminated								
Lever	213-177	0.09	227-176	0.09	208-144	-	234-155	-
Scheil	213-177	0.13	227-177*	0.09	208-97	0.01	234-109	-

*Note: During Scheil solidification the remaining liquid phase is depleted of Cu which results in that the final freezing occurs at the temperature of the Ag-Pb-Sn eutectic.

Table 4: Sequence of phase formation during lever rule and Scheil freezing without and with Pb-contamination.

	Lever rule	T (°C)	Scheil	T (°C)
Sn-3.5Ag				
Solder	$L \rightarrow (Sn) + \epsilon$	221	$L \rightarrow (Sn) + \epsilon$	221
Contaminated	$L + (Sn)$	213	$L \rightarrow (Sn)$	213
	$L + (Sn) + \epsilon$	211	$L \rightarrow (Sn) + \epsilon$	211
	$(Sn) + \epsilon + (Pb)$	177	$L \rightarrow (Sn) + \epsilon + (Pb)$	177
Sn-4Ag-1Cu				
Solder	$L + \eta$	225	$L \rightarrow \eta$	225
	$L + \eta + \epsilon$	221	$L \rightarrow \eta + \epsilon$	221
	$(Sn) + \eta + \epsilon$	215	$L \rightarrow (Sn) + \eta + \epsilon$	215
Contaminated	$L + \eta$	227	$L \rightarrow \eta$	227
	$L + \eta + \epsilon$	210	$L \rightarrow \eta + \epsilon$	210
	$L + \eta + \epsilon + (Sn)$	208	$L \rightarrow \eta + \epsilon + (Sn)$	208
	$(\eta \rightarrow \eta')$		$(\eta \rightarrow \eta')$	
	$L + \eta' + \epsilon + (Sn)$	187	$L \rightarrow \eta' + \epsilon + (Sn)$	187
	$\eta' + \epsilon + (Sn) + (Pb)$	176	$L \rightarrow \epsilon + (Sn) + (Pb)$	177
Sn-3.5Ag-4.8Bi				
Solder	$L + \epsilon$	215	$L \rightarrow \epsilon$	215
	$L + \epsilon + (Sn)$	214	$L \rightarrow \epsilon + (Sn)$	214
	$\epsilon + (Sn)$	201		
Contaminated	$L + (Sn)$	208	$L \rightarrow (Sn)$	208
	$L + (Sn) + \epsilon$	207	$L \rightarrow (Sn) + \epsilon$	207
	$L + (Sn) + \epsilon + (Pb)$	154	$L \rightarrow (Sn) + \epsilon + (Pb)$	146
	$(Sn) + \epsilon + (Pb)$	144	$L \rightarrow (Sn) + \epsilon + (Pb) + (Bi)$	97
Sn-3.4Ag-1Cu-3.3Bi				
Solder	$L + \eta$	233	$L \rightarrow \eta$	233
	$L + \eta + (Sn) + \epsilon$	212	$L \rightarrow \eta + (Sn) + \epsilon$	212
	$\eta + (Sn) + \epsilon$	204	$(\eta \rightarrow \eta')$	
			$L \rightarrow \eta' + (Sn) + \epsilon$	187
			$L \rightarrow \eta' + (Sn) + \epsilon + (Bi)$	137
Contaminated	$L + \eta$	234	$L \rightarrow \eta$	234
	$L + \eta + (Sn)$	206	$L \rightarrow \eta + (Sn)$	206
	$L + \eta + (Sn) + \epsilon$	205	$L \rightarrow \eta + (Sn) + \epsilon$	205
	$(\eta \rightarrow \eta')$		$(\eta \rightarrow \eta')$	
	$L + \eta' + (Sn) + \epsilon$	187	$L \rightarrow \eta' + (Sn) + \epsilon$	187
	$L + \eta' + (Sn) + \epsilon + (Pb)$	165	$L \rightarrow \eta' + (Sn) + \epsilon + (Pb)$	160
	$\eta' + (Sn) + \epsilon + (Pb)$	155	$L \rightarrow \eta' + (Sn) + \epsilon + \theta$	136

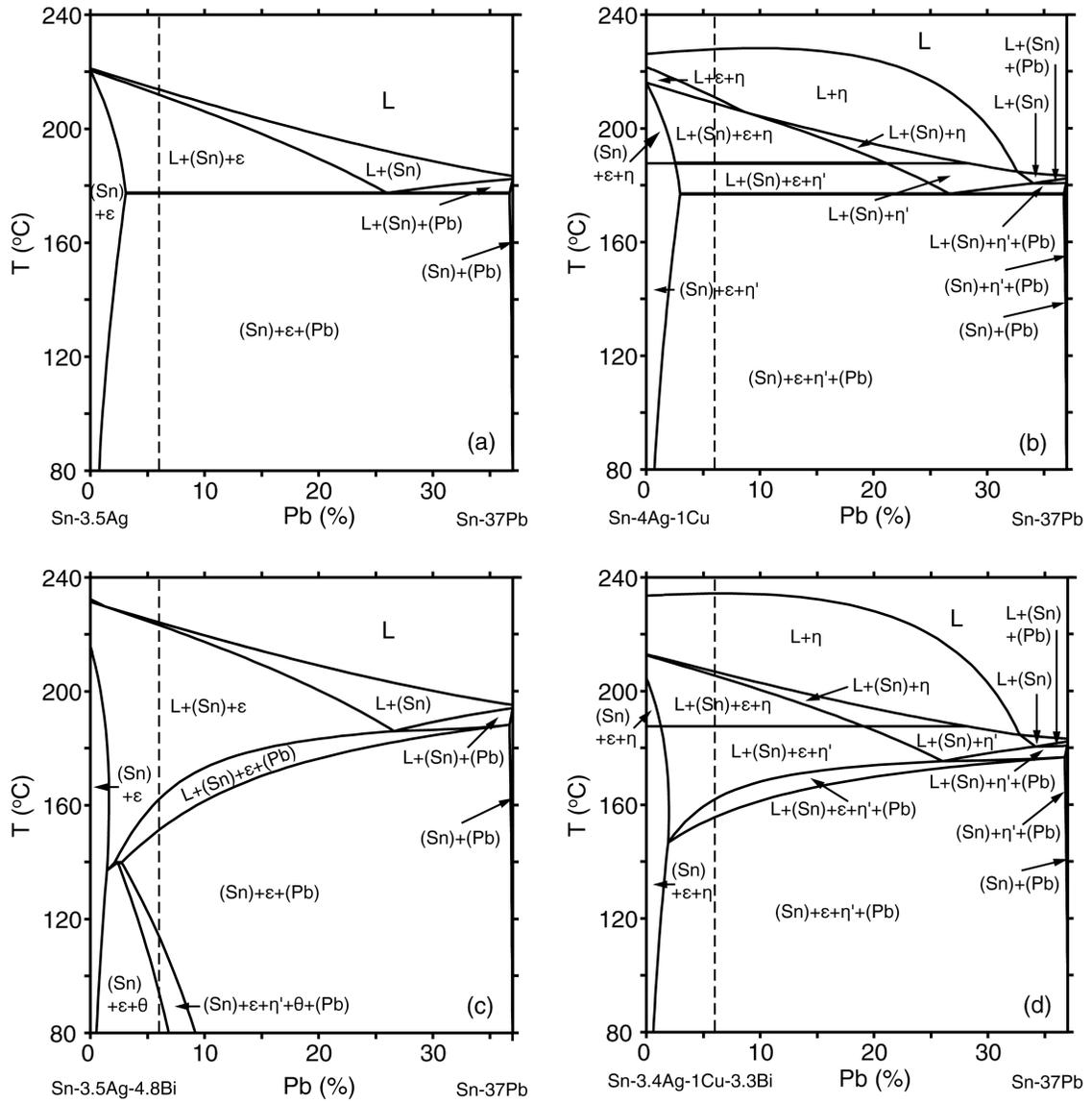


Figure 1: Isopleths from the original solder composition to the composition of the contaminant. (a) Sn - 3.5 % Ag to Sn - 37 % Pb, (b) Sn - 4 % Ag - 1 % Cu to Sn - 37 % Pb, (c) Sn - 3.5 % Ag - 4.8 % Bi to Sn - 37 % Pb, (d) Sn - 3.4 % Ag - 1 % Cu - 3.3 % Bi to Sn - 37 % Pb. The dotted lines represent a Pb concentration of 6 %.

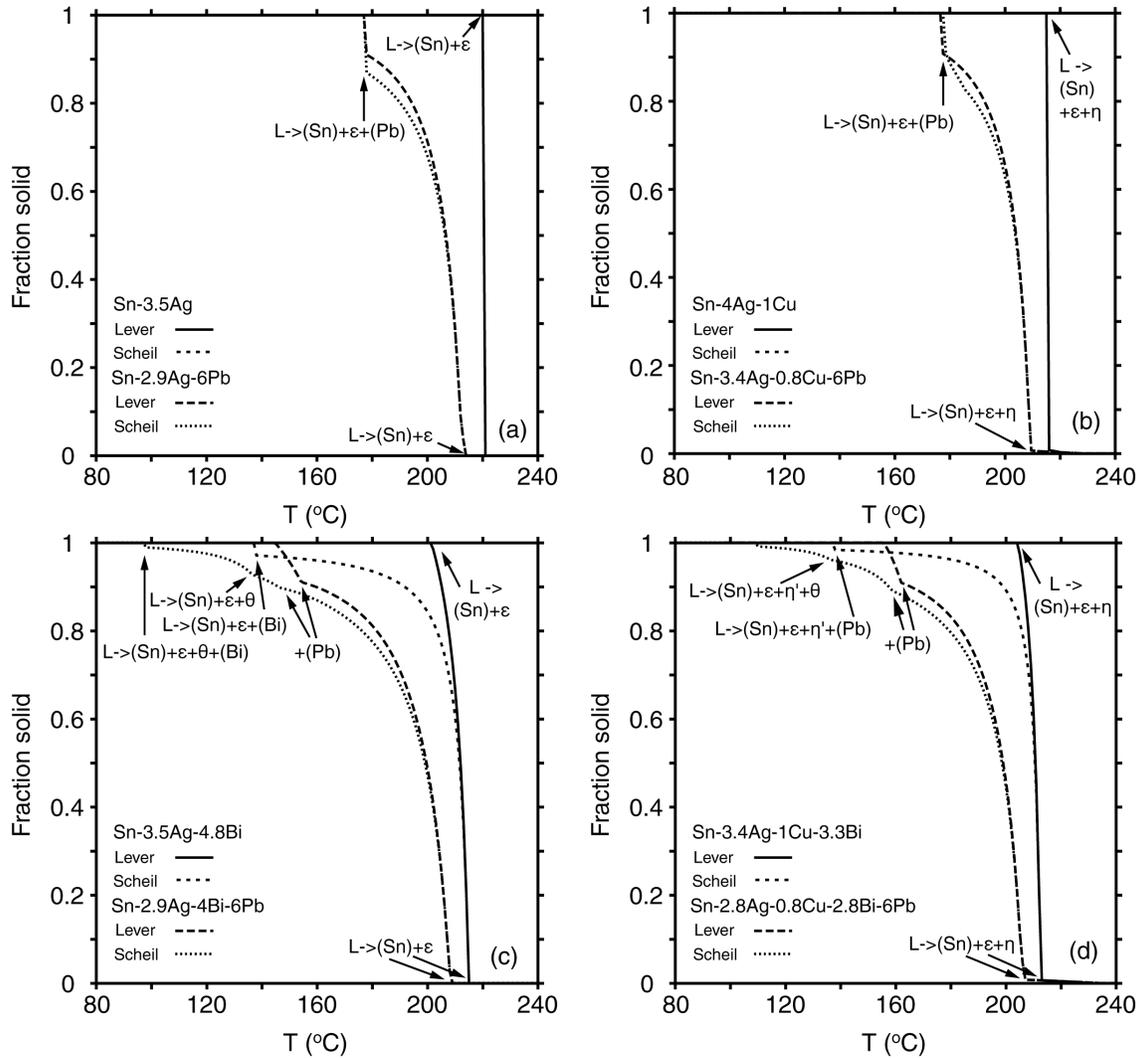


Figure 2: Calculated fraction solid vs. temperature curves from lever rule and Scheil calculations for the pure and contaminated solder alloys. (a) Sn - 3.5 % Ag and Sn - 2.9 % Ag - 6 % Pb, (b) Sn - 4 % Ag - 1 % Cu and Sn - 3.4 % Ag - 0.8 % Cu - 6 % Pb, (c) Sn - 3.5 % Ag - 4.8 % Bi and Sn - 2.9 Ag - 4 Bi - 6 % Pb, (d) Sn - 3.4 % Ag - 1 % Cu - 3.3 % Bi and Sn - 2.8 % Ag - 0.8 % Cu - 6 % Pb.