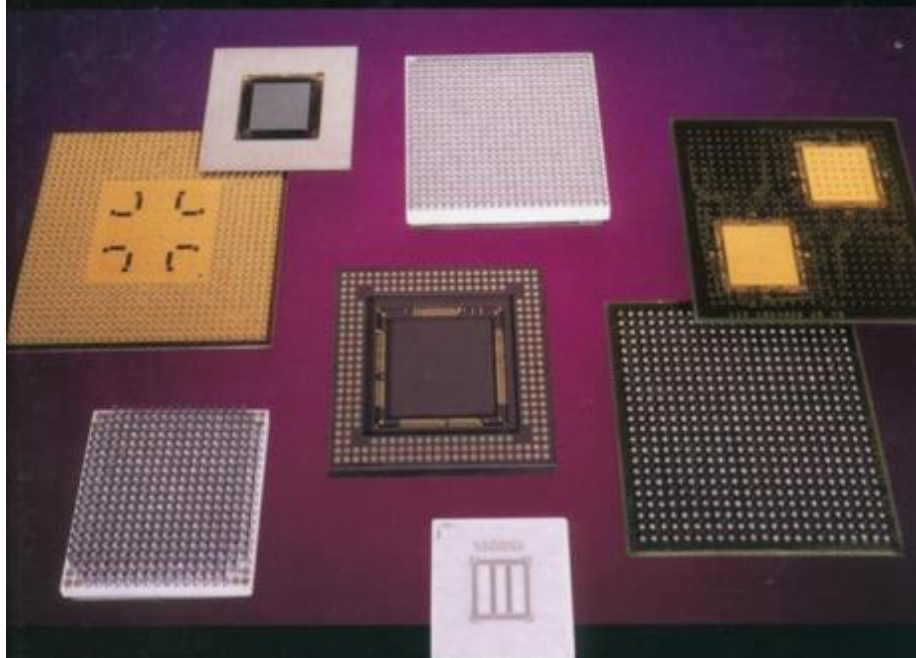


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Modern Solder Technology for Competitive Electronics Manufacturing

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The detailed correlation will be discussed in Chap. 10. The general guidelines in separating the types or requirements of solders for the corresponding land patterns are

Standard 50- to 25-mil (0.050- to 0.025-in or 1.25- to 0.63-mm) pitch

25- to 15-mil (0.025- to 0.015-in or 0.63- to 0.38-mm) pitch

15- to 8-mil (0.015- to 0.008-in or 0.38- to 0.20-mm) pitch

Soldering is also distinguished by the type of chemistry or cleaning process. The chemistry of a flux/vehicle system and the after-soldering cleaning follow the same selection rules. Three main chemistries are mildly activated rosin- (RMA)-chemistry with solvent cleaning, water-soluble chemistry with water cleaning, and no-clean chemistry without cleaning.

3.2 Physical Properties

Although other properties can be contributing factors to the overall performance of solders, five physical properties are discussed in this section because of their special importance to today's and future electronic packaging and assembly:

- Phase transition temperature
- Electrical conductivity
- Thermal conductivity
- Coefficient of thermal expansion
- Surface tension

3.2.1 Phase transition temperature of common solder alloys

An *alloy* is a metallic material which is formed from mixing a combination of two or more elements in the liquid state and then allowing them to solidify into the solid state. The elements in an alloy system may have a different extent of mutual miscibility in either the liquid or solid state. The thermodynamic interaction between elements results in the complete, partial, or nil miscibility which in turn may form metallurgical phases. Generally, the resulting alloys fall into one of the following categories:

- Complete miscibility in solid and liquid states
- Complete miscibility in liquid state and partial miscibility in solid state
- Complete miscibility in liquid state and no miscibility in solid state
- Systems with formation of intermediate phases or intermetallic compounds

For practical applications, three distinct temperatures are often used:

- *Solidus temperature.* The temperature below which the solid phase is stable (above the solidus temperature, material consists of a liquid phase and solid phase).
- *Liquidus temperature.* The temperature above which the liquid phase is stable.
- *Plastic range.* The temperature range between liquidus and solidus for a given composition at which the alloy is neither solid nor liquid.
- *Eutectic temperature.* The temperature at which a single liquid phase is transformed into two solid phases.

Table 3-1 summarizes these important temperatures for common solder alloy compositions. To facilitate practical use, Table 3-1 is segmented according to fourteen alloy systems. Table 3-2 lists the solder alloys covered by the most current version of the American National Standards Institute (ANSI) J-STD-006 Interim Final Issue "General Requirements and Test Methods for Electronic Grade Soft Solder Alloys and Fluxed and Non-fluxed Solid Solders for Electronic Soldering Applications." Further discussion on standards and specification are covered in Chap. 17.

3.2.2 Electrical conductivity

3.2.2.1 Basic theory. By definition, electrical conductivity is the result of movement of electrically charged electrons or ions from one location to another under an electric field. The electron conductivity is primarily predominant in metals, whereas ionic conductivity is responsible for the conductivity of oxides and nonmetallic materials. The characteristics of electrical conductivity can be described in terms of electron energy band structure as shown in Fig. 3-1. For metals, there is a partially filled electron band or a finite concentration of electrons in the conduc-

Table 3-1. Phase Transition Temperatures of Solder Alloys

Alloy composition	Solidus		Liquidus		Plastic range	
	°C	°F	°C	°F	°C	°F
Sn-Pb System						
100 Sn	232	450	232	450	0	0
80 Sn/20 Pb	183	361	199	390	0	0
70 Sn/30 Pb	183	361	193	380	10	19
63 Sn/37 Pb (E)	183	361	183	361	0	0
60 Sn/40 Pb	183	361	190	375	7	14
50 Sn/50 Pb	183	361	216	420	33	59
40 Sn/60 Pb	183	361	238	460	55	99
30 Sn/70 Pb	185	365	255	491	70	126
25 Sn/75 Pb	183	361	266	511	83	150
15 Sn/85 Pb	183	361	288	550	105	189
10 Sn/90 Pb	268	514	302	575	34	61
5 Sn/95 Pb	308	586	312	594	4	8
100 Pb	328	620	328	620	0	0
Sn-Ag System						
100 Ag	961	1761	961	1762	0	0
96.5 Sn/3.5 Ag (E)	221	430	221	430	0	0
95 Sn/5Ag	221	430	240	464	19	34
Sn-Sb System						
100 Sb	630.5	1167	630.5	1167	0	0
99 Sn/1 Sb (E)	235	456	235	456	0	0
95 Sn/5 Sb	235	455	240	464	5	9
Sn-Bi System						
100 Bi	271.5	520	271.5	520	0	0
42 Sn/58 Bi (E)	138	281	138	281	0	0
Sn-In System						
100 In	156.6	313	156.6	313	0	0
70 Sn/30 In	117	241	175	346	58	105
52 Sn/48 In	118	244	131	268	13	24
60 Sn/40 In	113	235	122	252	9	17
48 Sn/52 In (E)	117	241	117	241	0	0
Pb-In System						
70 Pb/30 In	240	464	253	488	13	24
50 Pb/50 In	180	256	209	408	29	52
40 Pb/60 In	174	345	185	365	11	20
30 Pb/70 In	160	320	174	345	14	25

13

Special Topics in Soldering-related Issues

13.1 Intermetallics Versus Solder Joint Formation

Intermetallics can be beneficial or detrimental to the formation of solder joints and their long-term reliability. Relating to electronics packaging and assembly, intermetallic compounds may come from one or more of the following processes and sources:

- Intermetallics are formed at the solder-substrate interface during soldering.
- Intermetallics are present in the interior of the solder joint as the inherent metallurgical phases of a given solder composition, such as 95 Sn/5 Sb and 96 Sn/4 Ag.
- Intermetallics are developed during a service life either along the interface and/or in the interior of the solder joint.

Metallurgically, an intermetallic compound is one type of intermediate phase that is a solid solution with intermediate ranges of composition. Intermetallic compounds may form when two metal elements have a

limited mutual solubility. These compounds possess new compositions of a certain stoichiometric ratio of the two component elements for a binary system.

The new phases have different crystal structures from those of their elemental components. The properties of the resulting intermetallic compounds generally differ from those of the component metal, exhibiting less metallic characteristics, such as reduced ductility, reduced density, and reduced conductivity. Since the tin in a tin-lead solder reacts with most metals that are commonly used in electronics packaging and assembly, the presence and formation of intermetallic compounds are expected. In addition, the indium in indium-based solders is also readily reactive with copper, gold, and silver. The existence of intermetallic compounds has been observed at or near the interface of the solder and substrate as well as in the bulk of the solder joint.

By using phase diagrams, the potential formation of the intermetallics and their extent between known compositions of solder and substrates can be anticipated. Table 13-1 lists the compounds that have been identified and established under the equilibrium condition for common substrate metals in contact with tin-based and indium-based solders. It should be noted that the thermodynamically stable com-

Table 13-1. Thermodynamically Stable Intermetallic Compounds

Solder	Substrate	Intermetallic compounds
Sn-based	Au	AuSn, AuSn ₂ , AuSn ₄
Sn-based	Ag	Ag ₃ Sn
Sn-based	Cu	Cu ₃ Sn, Cu ₅ Sn ₈ , Cu ₃ Sn, Cu ₆ Sn ₅
Sn-based	Pd	Pd ₃ Sn, Pd ₂ Sn, Pd ₅ Sn ₂ , PdSn, PdSn ₂ , PdSn ₄
Sn-based	Ni	Ni ₃ Sn, Ni ₃ Sn ₂ , Ni ₃ Sn ₄
Sn-based	Pt	Pt ₃ Sn, PtSn, Pt ₂ Sn, PtSn ₂ , PtSn ₄
Sn-based	Fe	FeSn, FeSn ₂
In-based	Au	AuIn, AuIn ₂
In-based	Ag	Ag ₃ In, AgIn ₂
In-based	Cu	Cu ₃ In, Cu ₅ In ₄
In-based	Pd	Pd ₃ In, Pd ₂ In, PdIn, Pd ₂ In ₃
In-based	Ni	Ni ₃ In, NiIn, Ni ₂ In ₃ , Ni ₃ In ₇
In-based	Pt	Pt ₂ In ₃ , PtIn ₂ , Pt ₃ In ₇

Table 13-2. Formation of Intermetallic Compounds on Cu and Ni Substrates⁴

Solder composition	At interface		In the bulk of solder	
	Cu	Ni-plating	Cu	Ni-plating
5 Sn/95 Pb	Cu ₃ Sn	Ni ₃ Sn ₄	0	0
5 Sn/92.5 Pb/2.5 Ag	Cu ₆ Sn ₆	Ni ₃ Sn ₂	Ag ₃ Sn	Ag ₃ Sn
92 Sn/8 Sb	Cu ₃ Sn, Cu ₆ Sn ₅	Ni ₃ Sn ₄	Cu ₆ Sn ₅	(NiCu) ₃ Sn
65 Sn/25 Ag/10 Sb	Cu ₃ Sn, Cu ₆ Sn ₅	Ni ₃ Sn ₄	Ag ₃ Sn, CuSn	Ag ₃ Sn, (NiCu) ₃ Sn

thinner layer compared with the clean surfaces under otherwise identical conditions. Furthermore, it was found that the composition formed may vary with the surface condition and the availability of the tin content; for example, 5 Sn/95 Pb on a clean nickel surface, produced Ni₃Sn₄ intermetallics, while on an oxidized surface it resulted in the formation of Ni₃Sn₂. This is primarily attributed to the lower availability and less accessibility of tin to the oxidized surface. Comparing a high-lead solder (5 Sn/92.5 Pb/2.5 Ag) with a high-tin solder (65 Sn/25 Pb/10 Sb) on a nickel surface, different morphologies of intermetallics are detected; high-lead solder is associated with small, round intermetallic crystallites (Ag₃Sn) and high-tin solder with large, needlelike crystallites.

The effect of the reflow condition was studied by prolonging the dwell time at the peak temperature. Figure 6-14 is an SEM micrograph showing the microstructural development and intermetallic formation of 63 Sn/37 Pb solder on a Cu substrate under an extreme reflow condition that imposes a dwell time at peak temperature 3 times longer than that of a normal process, as shown in Fig. 6-13. The prolonged heating at peak temperature resulted in the development of a much coarser microstructure and a needle-shaped phase that is identified as Cu-Sn intermetallics by x-ray energy dispersion analysis as shown in Fig. 6-15. The examination of the cross section of the solder joint confirmed that intermetallics have moved away from the interface area and are distributed throughout the bulk of the solder joint.

In summary, the extent of intermetallic formation, the composition of intermetallic compounds and the morphology of intermetallics depend on internal as well as external factors. These include

- Metallurgical reactivity of solder composition with substrate
- Soldering (reflow) peak temperature
- Dwell time at peak temperature

- Surface condition of substrate—clean versus oxidized
- Solder composition
- Postsoldering storage conditions
- Service condition

As to the role of intermetallics at the interface or in the interior, beneficial or detrimental, it depends on some specific factors. Solder wetting on the substrate followed by the formation of a thin layer of intermetallic is a prevalent mechanism for solder to make a permanent bond with the substrate. Figure 13-5 shows the bonding layer between the 63 Sn/37 Pb solder and the substrate. However, as the intermetallic layer becomes thicker, adverse effects may result. The generally accepted thickness falls in the range of 1 to 5 μm .

The intermetallics in the bulk of the solder joint (away from the interface) may also play a positive or negative role. A proper morphology, size, and distribution of intermetallics in solder may act as a strengthening phase; in contrast, large needle-shaped compounds generally weaken the mechanical properties of the solder joint.

The formation of excessive intermetallic compounds has been demonstrated as one of the most likely sources of solder joint failure. When an appreciable amount of intermetallics is developed along the solder-substrate interface, cracks are often initiated around the interfacial area under stressful conditions. Figure 13-6 shows the development of Cu-Sn intermetallics after the solder joint of 96.5 Sn/3.5 Ag on Cu has been subjected to service life in an automobile under-the-hood application.⁵ As can be seen, an extensive amount of needle-shaped intermetallics have formed. For the same assembly, solder joint cracking was detected near the solder joint interface, as shown in Fig. 13-7.



Figure 13-5. Bonding layer between solder and the substrate.

The adverse effect of intermetallic compounds on solder joint integrity is believed to be attributed to the brittle nature of such compounds and to the thermal expansion property, which normally differ from the bulk solder. The differential thermal expansion could contribute to internal stress development. In addition, excessive intermetallic compound which forms at the coating and substrate interface may impair the solderability of surfaces where the intermetallic compound depletes one element of the contact surface. One example is Sn depletion from the Sn-Pb coating on Cu leads, which causes the exposure of Sn-Cu intermetallic compound to oxidation, resulting in poor solderability of the component leads. In this case, the interface area is expected to have Cu_3Sn phase next to the copper substrate, followed by a Cu_6Sn_5 phase and a Pb-rich phase.

Excessive intermetallics may also alter the appearance of the solder joint, giving it a dull and rough surface. Figure 13-8 is the SEM micrograph of the free surface of a 63 Sn/37 Pb solder joint containing an excessive amount of intermetallics; the solder joint visually appears dull. In comparison, the shiny solder joint surface correlates with the SEM microstructure as shown in Fig. 13-9.

A newly developed process illustrates another positive role of intermetallics. A bonding process involves in situ formation of Cu-Sn intermetallics from a vapor-deposited Cu-Sn multilayer.⁶ The unique features of the process are its controlled intermetallic bonding thickness and its fluxless nature. The process successfully bonds the die and the metallized substrate. In the process, the die is composed of a multilay-

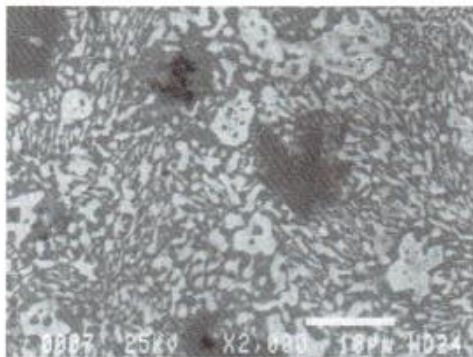


Figure 13-8. SEM micrograph of free surface of 63 Sn/37 Pb solder joint containing excessive intermetallics.