Chapter

5

Solder Technologies for Electronic Packaging and Assembly

Jennie S. Hwang
H–Technologies Group, Inc.
Cleveland, Ohio

5.1 Introduction

5.1.1 Scope

What drives the end-use market are the continued convergence of computing, communication, and entertainment as well as the relentless growth of the wireless, portable, handheld digital electronics and optoelectronics. On the ever-changing technology landscape, the industry has responded and will continue to respond to competitive demands in the global marketplace. New electronic gadgets will be featured with increasingly higher functionality, further simplicity, lower cost, and greater operational ease. What has transpired from these market demands is continued technological innovation and an ever-shortening product life cycle. Environment-friendly manufacturing and the delivery of environmentally benign end-use products that are ultimately safe at the end of the product life cycle will become essential to technology-business competitiveness. This is a continuing challenge to the industry. Solder has served as the interconnecting material for all three levels of connections: die, package, and board assembly. In addition, tin/lead solder is commonly used as a surface coating for component leads and PCB surface finishes. In addition to solder materials, the process used to form solder joints to accomplish the vital function of electrical, thermal, and mechanical linkages between two metallic surfaces is equally important.

This chapter addresses solder technologies in both material and process aspects for electronic packaging and assembly. Considering the established role of lead (Pb) and the demand in Pb-free materials, solder can be classified as either lead-containing or lead-free. In light of the global environmental commitment, this chapter will also cover Pb-free materials in terms of their properties and characteristics that are important to their applications in electronic packaging and assembly.

5.1.2 Surface mount technology

In this electronic and information age, we witness new technology developments and new product introductions to the marketplace almost on a monthly basis. One of the strongest trends, however, in the electronics interconnection and packaging segment is utilization of the surface-mounting concept to develop superior circuit board assemblies in both performance and cost. This concept has been utilized in hybrid assembly since the 1960s by interconnecting chip resistors, chip capacitors, and bare semiconductor dies on metallized substrates. Nevertheless, the potential of surface mounting was not fully explored and utilized until the early 1980s.

What is surface-mount technology? As the name implies, it is basically the application of science and engineering principles to board-level assembly by placing components and devices on the surface of the printed circuit board instead of through the board. Although this concept appears to be straightforward, the impact on the production floor is enormous, not only on components and design but also on materials and equipment. It also narrows the distinction between hybrid circuit assembly and printed circuit assembly. The specific benefits of surface mount technology in relation to through-hole technology include

- Increased circuit density
- Decreased component size
- Decreased board size
- Reduced weight
- Shorter leads
- Shorter interconnection
- Improved electrical performance
- Facilitated automation
- Lower costs in volume production

5.1.3 Industry trends

5.1.3.1 Semiconductors. Looking at the hierarchy of electronics, semiconductor devices have continuously exhibited improved reliability, reduced feature size, increased wafer size, and doubled complexity every 18 months, in accordance with the Moore's law. As examples, wafer size increased from 3 to 4 in (75 to 100 mm) in the 1980s to 12 in (300 mm) this year; circuits have shrunk to submicrometer (0.1 to 0.25 μm) from several micrometers; IC pin count has increased from 40 to 80 to more than hundreds or tens of hundreds; IC fabrication techniques and equipment are developing in rapid pace from wet process and microanalysis to X-ray lithography and nanoanalysis.

At 45 years old, integrated circuits (ICs) are moving into another era of major developments. The new copper interconnect technology facilitates the implementation of deep submicron circuitry thus alleviating the RC delay problem. Copper has a significantly better conductivity than aluminum, which has been the backbone of IC circuits (Cu = 1.7 μΩ-cm; Al = 3.1 μΩ-cm). Copper is also known to have better electromigration resistance than aluminum. However, copper diffusion into silicon has been one of the major obstacles to the use of copper interconnect. Using IBM's proprietary barrier layer to prevent copper diffusion along with other companion technologies, the copper interconnect has become increasingly prevalent since 1999. IBM's Cu-connect ASIC technology (SA-12) also demonstrated 40 percent power savings by using 1.8 V rather than 2.5 V. The reduction in power consumption without sacrificing signal-to-noise quality is critical to the performance of portable electronics.

For example, it is reported that interconnects account for more than 70 percent of the signal delay in a 0.25-μm chip. Interconnect RC delay increases as the square of the minimum feature size, thus determining the IC chip performance. As the feature size continues to shrink to 0.13 μm or finer, RC delay issues become more critical.

In addition to the lower resistance offered by copper, a capacitance dielectric material lower than SiO_2 is equally important to keep the interconnect RC delay in control for the nanoelectronics era. *System-on-a-chip* is another ongoing development. Fundamentally, the material innovations will be paramount to future generations of IC circuits. Combining deeper understanding in materials science with technology development, silicon crystals will get closer to perfection. Perfect silicon, obtained by eliminating crystal defects such as vacancies and dislocations, offers a new level of performance. Other silicon technologies continue to advance. IBM's *strained silicon* technology is reported to increases chip speed up to 35 percent while reducing power consumption without needing to shrink silicon circuits. The new strained silicon technology speeds the flow of electrons through transistors by stretching the material. The stretching concept may not be new, but the know-how to manufacture chips from this concept is a breakthrough. The process may seem simple enough, like stretching fabric, but the novelty is at the atomic level where one manipulates the atoms in silicon.

Up to now, electrons have been the workhorses for the electronic age and information era, making possible all modern products from ovens and cameras to computers and cell phones. Future technology may not only be derived from the conventional material theories of circuits, based on the mobility and conductivity of electrons and phonons, but also from photons. Nonetheless, electron transport will remain the main power behind future products in the foreseeable future.

5.1.3.2 IC packaging and passive components. With the known good die being a lingering issue for the board level assembly, the use of packaged surface mount devices continues to dominate. Across the two decades, the industry has evolved from dual in-line packages (DIPs) and pin grid arrays (PGAs) to 50-mil surface leadless ceramic chip carriers (LCCCs), plastic leaded chip carriers (PLCCs), small outline IC (SOIC), chip-scale packages (CSPs), and fine pitch quad flat pack (QFP), thin quad flat pack (TQFP), and array packages such as ball grid arrays (BGAs). The implementation of fine-pitch BGAs and CSPs continues to increase. Scanning over the package evolution, it can be categorized in three generic groups: Through-hole, surface mount, and chip-scale/direct die attach.

The use of surface mount devices finally exceeded that of through-hole devices in 1995, as shown in Fig. 5.1. It is projected that SMT will continue to enjoy a healthy growth rate at the expense of through holes, and the introduction of chip-scale (size) packages and direct chip attach will slowly fill the niche areas that require either maximal density and speed or minimal size and weight. Various packages are differentiated from one another by virtue of functional capabilities and/or physical characteristics. For example, package height of through-hole PGA in 3.5 mm compares with BGA in 2.3 mm; package-to-die size ratio for PQFP is around 8, and TBGA around 5. IC packages having high pin counts and new designs are expected to proliferate. Nonetheless, it is interesting to note that, despite the frequent introduction of new packages, SOIC/TSOP IC packages still occupy the largest market share at the present time and perhaps in the foreseeable future.

Array packages are primarily driven by high I/O count, board area savings, and the high radio frequencies required for wireless communication products.

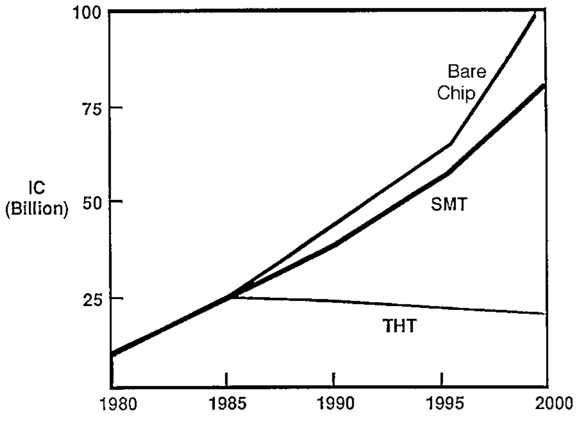


Figure 5.1 Market share of surface mount vs. through-hole.

The I/O pitch of BGAs generally falls in the range of 1.00 to 1.50 mm (0.040 to 0.060 in). PBGA, TBGA, and CBGA all have been adopted by chip makers for the high I/O counts required in workstations and minicomputers. Considering all factors in performance, economics, and reliability, a 250 I/O count is considered to be a break point in selecting between QFP and BGA. For products in which size and weight are critical to their marketability, CSP has been the center of attention since 1997. All six main CSP technologies (wire bond/rigid interposer, wire bond/flex interposer, flip-chip/rigid interposer, flip-chip/flex interposer, lead-frame/chip on lead, and wafer-level packaging) have been put to use.

The relative size of CSPs in comparison with other SMT packages can be clearly represented by the package area/die area ratio. CSP is generally accepted as less than 1.5, as opposed to BGA (1.25 mm pitch) $\cong$ 4, BGA (1.00 mm pitch) $\cong$ 2, QFP (0.4 mm pitch) $\cong$ 7, and QFP (0.5 mm pitch) $\cong$ 9.0. CSPs have made today's smaller portable electronics possible.

In addition to portable consumer electronics, the notebook computer is another application that drives the use of CSPs for relatively higher-I/O ASIC chips. CSPs have also been utilized in flash memory chips and extended to DRAM and SRAM packaging. However, the requirement of high-density PCB routing and the limited availability of package substrate materials have prevented the growth of high-I/O CSP technology to its fullest potential. The majority of CSPs have been for low-I/O applications. While a few specific CSP designs have emerged as "winners," the proliferation of new designs continues. As a renewed interest, flip-chip (wherein a bare chip with solder bumps on its surface is turned upside down and bonded directly onto the substrate without lead frame and wire bonding) has served as one of the base technologies to achieve chip-size packages, although CSPs can also be accommodated by wire bonding. As IC packages in conventional molded form or in chip size (scale) packages, or in flip-chip or in other advanced designs, are proliferating, the selection among various packages largely depends on the speed, heat dissipation, density (I/O), and cost desired. It is also end-use driven. For example, in the near future, while automotive ICs will use flip-chips and BGAs with high input/output (I/O), mobile and wearable electronics resort to ultra-thin CSP packages, stacked-chip packages, and system-in-package designs. Such packages will reach a higher performance level. Instead of 0.8-mm thickness, thinner CSP packages with a 0.5 mm thickness will be in demand. For stacked-chip packages, the goal is to put an entire cell phone in a single stacked package containing three vertically mounted dice. Because of heat management considerations, stacked-chip packages will remain limited in memory and other low-power uses in the near future.

In parallel, microelectromechanical systems (MEMS) will evolve by adding optical or mechanical components to a package, expanding the current end uses beyond vehicle airbag sensors, printer ink jet heads, and accelerometers. In this area, wireless applications will top the development list—for example, MEMS RF switches because of their advantage of low series resistance.

To meet wireless communications market demands, not only do IC packages need to be miniaturized, passive device manufacturers also must strive to meet requirements for minimal real estate through chip size reduction or integration. In addition to physical miniaturization, increased capacitance values are also desirable for enhanced performance. To control and reduce cost, base metal electrodes, replacing noble metals, will increasingly find acceptance. For high-frequency applications, sustained capacitance and low equivalent series resistance (ESR) are increasingly important performance criteria for capacitors. The materials and processes that enable thinner dielectric layers to achieve higher capacitance values also will see increased demand. Additionally, high-frequency radio frequency (RF) circuits can make use of low-temperature ceramic co-fired materials, as they can reduce crosstalk between circuit elements. To alleviate the supply and cost concerns, niobium may be employed as a replacement for tantalum in capacitors.

We should begin to see a significant increase in the use of small 0402 and 0201 chips. Complementing discrete packages, other options are to integrate resistors, capacitors, and inductors in one package or to share the same package with ICs through thin or thick film technologies.

5.1.3.3 Board-level assembly. Ongoing efforts will be made to maximize yield, minimize defect rates, and improve performance by utilizing the technical knowledge, state-of-art equipment, and materials that have evolved in the industry. Constant assessment of new IC packages in conjunction with board design will become a part of the board-assembly business. Solder paste will remain the primary interconnection material, characterized by its established infrastructures, metallic nature, and fitness for automated manufacturing. Solder paste will only work not for SMT interconnections but also for certain through-hole components (paste-in-hole). Other solder deposition techniques, including solder jetting, will be assessed for specific packaging and assembly operations. Automation, SMT fitness (e.g., pick-and-place operations), and cost will be the determining factors for the viability and vitality of any new technology.

With the introduction of new packages and the increased number of package types for the PCB assembly and manufacturing processes, reflow profile in particular warrants further attention. Reflow profile not only affects the production defects and yield, it has an impact on the overall reliability of the assembly. A slower heating rate (<2°C/sec, ideally <1°C/sec in preheating zone) in conjunction with lower peak temperature exposure produces a good reflow profile. The same principle should also apply to rework and repair; using preheating and top/bottom heat source will facilitate the process and minimize any damage that may occur during rework. BGA rework processes and procedures are being established. The role of inert atmosphere (N_2) soldering using low-nitrogen-consumption reflow ovens will be more prominent.

The accuracy and speed of placement equipment continues to improve. In addition, “gentle” placement capability, which allows manufacturers to work with small and fragile CSPs, is also in demand, including reliable feeding mechanisms and vision capability. To handle CSPs of 0.50-mm (0.020-in) pitch or finer, positioning accuracy of ±0.05 mm (±0.002 in) is required. Printing and dispensing systems for applying solder paste, underfill, adhesives, and coatings are characterized by increased automation and precision. New functional features continue to emerge to facilitate production operation and to enhance the end results.

Overall, flexible processes, agile manufacturing, and infrastructures equipped with hardware that offer versatile process capabilities are critical to the future success of SMT manufacturing.

As the microelectronics and electronics industries continue to strive for higher quality and yield in every level of materials, designs, and processes, and as the density of board-level populations continues to increase, the demands on the soldering process and solder-paste materials will be increasingly stringent. Furthermore, environmentally friendly production will be a required part of future manufacturing. This includes CFC-free processes, reduced volatile organic compounds (VOCs), minimal waste, and lead-free solders.

In view of these trends, this chapter outlines the fundamentals of soldering and solder paste and the practical techniques and know-how in the key steps of soldering and solder-paste application, as well as new and emerging products and processes. It is hoped that this chapter will provide integrated knowledge in the soldering and solder-paste arena and stimulate much needed innovations in material, design, and processes.

5.1.4 Interdisciplinary and systems approach

It has been said that the best science and technology are produced by a combination of four elements: an overriding commitment to scientific excellence, vision, intuition, and initiative. Soldering and solder-paste technology is no exception. Therefore, the objective of researchers is to meet demands for versatility in the soldering process and in solder-paste materials, and to continue to add to the pool of technology by applying and utilizing fundamental sciences and technologies.

From a technology point of view, pastes come from the interplay of several scientific disciplines. Figure 5.2 illustrates the spirit of paste technology.[1] Based on this technology, a number of existing and potential application product lines can be derived. These product lines are composed of organopolymeric vehicles and metallic and nonmetallic particulates, ranging from PM injection molding to EMI shielding composites, cermet thick film, polymer thick film, and solder paste, brazing paste, and adhesives. While each of these product lines has its unique qualities, one common fundamental is paste technology. Sciences and technologies to be utilized in paste technology include metallurgy and particle technology, chemistry and physics, rheology, and formulation technology. In addition, to meet the demands of the ever-changing electronics packaging industry and the accelerating pace of developments, a collaborative effort among users, material suppliers, and equipment manufacturers is much needed. They must be involved from the design state onward so as to develop the best suitable product or process system.

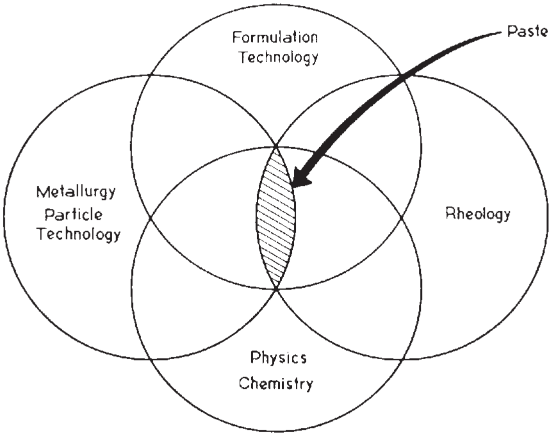


Figure 5.2 Market share of surface mount vs. through-hole.

5.2 Solder Materials

5.2.1 Solder alloys

Solders are generally described as fusible alloys with liquidus temperature below 400°C (750°F).

The elements commonly used in solder alloys are tin (Sn), lead (Pb), silver (Ag), bismuth (Bi), indium (In), antimony (Sb), and cadmium (Cd). Their melting points are listed in Table 5.1. In addition to tin-lead alloys, binary solder alloys include tin-silver, tin-antimony, tin-indium, tin-bismuth, lead-indium, and lead-bismuth. Ternary alloys include tin-lead-silver, tin-lead-bismuth, and tin-lead-indium. The basic alloy for solder bumps at the die level (particularly the flip-chip) contains high temperature, high lead compositions such as Sn5/Pb95 or Sn10/Pb90. Eutectic or near-eutectic alloys such as Sn60/Pb40, Sn62/Pb36/Ag2, and Sn63/Pb37, have also been used successfully. The solder bump on the underside of the carrier CSP/BGA substrate, for example, can either be high temperature, high lead or eutectic, near eutectic tin/lead or tin/lead/silver materials.

TABLE 5.1 Melting Points of Common Solder Elements

	Sn	Pb	Ag	Bi	In	Sb	Cd
°C	232	328	961	271.5	156.6	630.5	321.2
°F	450	620	1762	520	313	1167	610

Because of the temperature tolerance level of conventional board materials such as FR-4, board-level solder for attaching components and IC packages is limited to eutectic, near-eutectic tin/lead, and tin/lead/silver solders. In some cases, tin/silver eutectic and low-temperature solder compositions containing bismuth (Bi) or indium (In) have been used.

Solder can be applied in various physical forms, including bar, ingot, wire, powder, preform, solder sphere and column, and paste, and in the molten state. The intrinsic properties of solder materials can be considered in three categories: physical, metallurgical, and mechanical. With the continued development of lead-free solders, new ternary, quartnary, and pentanary systems will proliferate.[2] The solidus and liquidus temperatures of some commonly used compositions are listed in Table 5.2.

Generally, the alloy selection is based on the following criteria:

- Alloy melting range in relation to service temperature
- Mechanical properties of the alloy in relation to service conditions
- Metallurgical compatibility, consideration of leaching phenomenon, and potential formation of intermetallic compounds
- Service environment compatibility, consideration of silver migration
- Wettability on specified substrate
- Eutectic versus noneutectic compositions

5.2.2 Metallurgy

For tin-lead binary alloys, the tin and lead elements have complete liquid miscibility and partial solid miscibility. The phase diagram in Fig. 5.3 shows solid solution regions represented by (Sn) and (Pb), a liquid region represented by L, liquid and solid solution regions represented by L + (Pb) and L + (Sn), and a solid solution mixture region, (Sn) + (Pb). As indicated, the eutectic point is 63 wt percent of Sn at a temperature of 183°C. The solubility of Sn in Pb increase as the temperature drops to the eutectic temperature and then decreases as

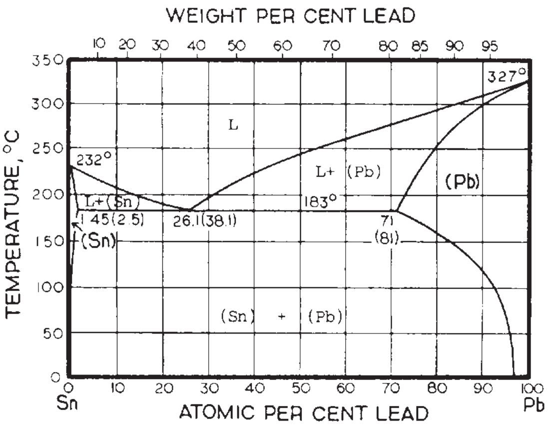


Figure 5.3 Phase diagram of Pb/Sn.

TABLE 5.2 Melting Range of Common Solder Alloys

	Melting range, solidus		Melting range, liquidus		Mushy range	
Alloy composition	°C	°F	°C	°F	°C	°F
70Sn/30Pb	183	361	193	380	10	19
63Sn/37Pb	183	361	183	361	0	0
60Sn/40Pb	183	361	190	375	7	14
50Sn/50Pb	183	361	216	420	33	59
40Sn/60Pb	183	361	238	460	55	99
30Sn/70Pb	185	365	255	491	70	126
25Sn/75Pb	183	361	266	511	83	150
10Sn/90Pb	268	514	302	575	34	61
5Sn/95Pb	308	586	312	594	4	8
62Sn/36Pb/2Ag	179	355	179	355	0	0
10Sn/88Pb/2Ag	268	514	290	554	22	40
5Sn/95Pb	308	586	312	594	4	8
625Sn/36Pb/2.5Ag	179	355	179	355	0	0
10Sn/88Pb/2Ag	268	514	290	554	22	40
5Sn/90Pb/5Ag	292	558	292	558	0	0
5Sn/92.5Pb/2.5Ag	287	549	296	564	9	15
5Sn/93.5Pb/1.5Ag	296	564	301	574	5	10
2Sn/95.5Pb/2.5Ag	299	570	304	579	5	9
1Sn/97.5Pb/1.5Ag	309	588	309	588	0	0
96.5Sn/3.5Ag	221	430	221	430	0	0
95Sn/5Sb	235	455	240	464	5	9
42Sn/58Bi	138	281	138	281	0	0
43Sn/43Pb/14Bi	144	291	163	325	19	34
52Sn/48In	118	244	131	268	13	24
70In/30Pb	160	320	174	345	14	25
60In/40Pb	174	345	185	365	11	20
70Sn/18Pb/12In	162	324	162	324	0	0
90Pb/5In/5Ag	290	554	310	590	20	36
92.5Pb/51In/2.5Ag	300	572	310	590	10	18
97.5Pb/2.5Ag	303	578	303	578	0	0

the temperature continues to drop. The same applies to the solubility of Pb in Sn.

The maximum solubility of Pb is Sn is 2.5 wt percent; of Sn in Pb, it is 19 wt percent. During soldering, the molten solder alloy wets the substrate with the aid of fluxes. Since the metallic surfaces involved in soldering tend to get oxidized or tarnished, the wettability depends to a large extent on the chemistry and reactions of fluxes. Nonetheless, the wetting phenomenon follows the basic wetting principle. For a system at a constant temperature T and pressure P,

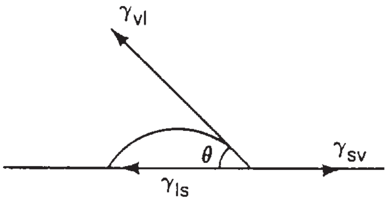
$$\left(\frac{\partial G}{\partial A}\right)_{PT} = \gamma$$

where G = free energy
A = area
γ = surface tension

Then, the thermodynamic condition for spreading to occur is

$$\Delta G < 0$$

The spreading of a liquid with negligible vapor pressure on a solid surface S is as follows:



Thus,

$$-\left(\frac{\partial G}{\partial A}\right)_{P,T} = \gamma_{sv} - (\gamma_{ls} + \gamma_{vl}\cos\theta)$$

where γ_{ls}, γvl, and γ_{sv} are liquid-solid, liquid-vapor, and solid-vapor interfacial tension, respectively. Therefore, for spreading to occur,

$$\gamma_{sv} - (\gamma_{ls} + \gamma_{vl}\cos\theta) > 0$$

or

$$\gamma_{sv} > \gamma_{ls} + \gamma_{vl}\cos\theta$$

In general, for a system with liquid to wet the solid substrate, spreading occurs only if the surface energy of the substrate to be wetted is higher than that of the liquid to be spread.

As the molten solder solidifies during cooling to form solder joints, the cooling process, including as the cooling rate, has a direct bearing on the resulting solder joint as to its microstructure and the development of voids. Figure 5.4 exhibits the SEM microstructure of 63 Sn/37 Pb melt under slow cooling, and Fig. 5.5 exhibits the microstructure under fast cooling, with other conditions being kept equal.

Because tin-lead solder alloys contain a solvus line and multiple solid phases, as shown in Fig. 5.3, they can be readily affected by heat treatment.

5.2.3 Solder powder[2]

Alloy powders can be produced by one of the common techniques—chemical reduction, electrolytic deposition, mechanical processing of solid particulates, and atomization of liquid alloys.

Alloy powders made from chemical reduction under high temperature are generally spongy and porous. The fine particles of noble metal powders are frequently precipitated by reduction of the salts in aqueous solution with proper pH. The precipitate slurry is then filtered, washed, and dried under highly controlled conditions. A mechanical method is generally used to produce flake-like particles. Metals possessing high malleability, such as gold (Au), silver (Ag), copper (Cu), and aluminum (Al), are most suitable for making flakes.

The electrolytic deposition process is characterized by dendrite particles, and it produces high-purity powders. The resulting particle sizes are affected by the type, strength, and addition rate of the reducing agent and by other re-

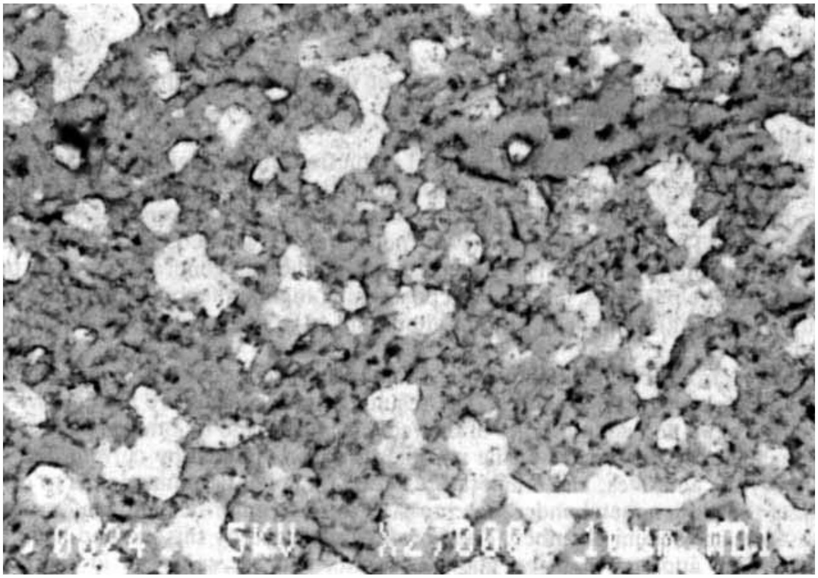


Figure 5.4 SEM micrograph of 63Sn/37Pb under slow cooling.

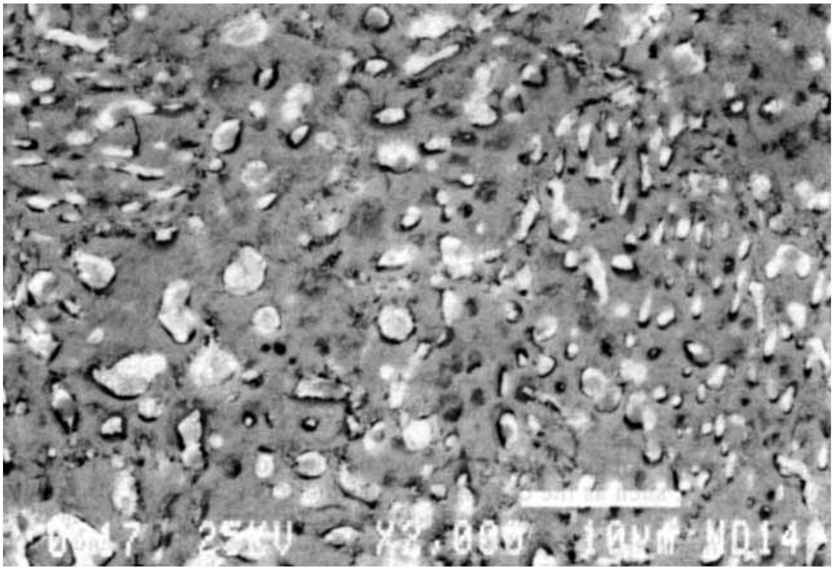


Figure 5.5 SEM micrograph of 63Sn/37Pb under fast cooling.

action conditions. The characteristics of the particles are also affected by current density, electrolytes, additives, and temperature. The principle of atomization is used to disintegrate the molten metal under high pressure through an orifice into water or into a gaseous or vacuum chamber. The powders produced by this method have relatively high apparent density, good flow rate, and are spherical in shape, as shown in Figs. 5.6 and 5.7. Powders to be used in solder paste are mostly produced by atomization because of its desirable inherent morphology and the shape of the resulting particles. Hence, the discussion that follows is concerned with the atomization technique only.

Figure 5.8 is a schematic of an inert gas atomization system with options of a bottom pouring system and a tilting crucible system. The system consists of a control cabinet, vacuum induction furnace, tundish, argon supply line, ring nozzle, atomization tower, cyclone, and powder collection container. The alloy is melted under inert gas at atmospheric pressure to avoid the evaporation of component ingredients. A high melt rate can be achieved. The molten material is then charged into the atomization tower. The melt is disintegrated into powder at atmospheric pressure by an energy-rich stream of inert gas. The process conducted in a closed system is able to produce high-quality powder.

In addition to inert gas and nitrogen atomization, centrifugal and rotating electrode processes have been studied extensively. The atomization mechanisms and the mean particle diameter are related to the operating parameters (diameter D, melting rate Q, and angular velocity ω of the rotating electrode) and to the material parameters (surface tension at melting point γ, dynamic viscosity η, and density at melting point ρ of the atomized liquid). The relationships among these parameters are presented subsequently.

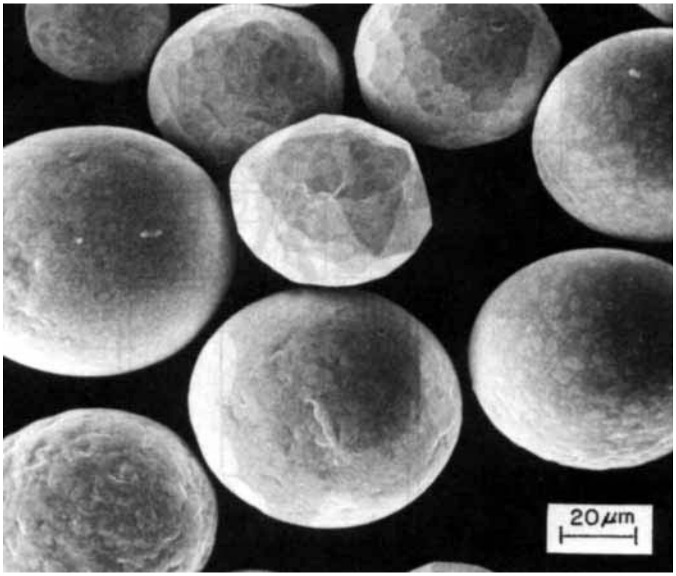


Figure 5.6 SEM micrograph of 63Sn/37Pb powder –200/+325 mesh.

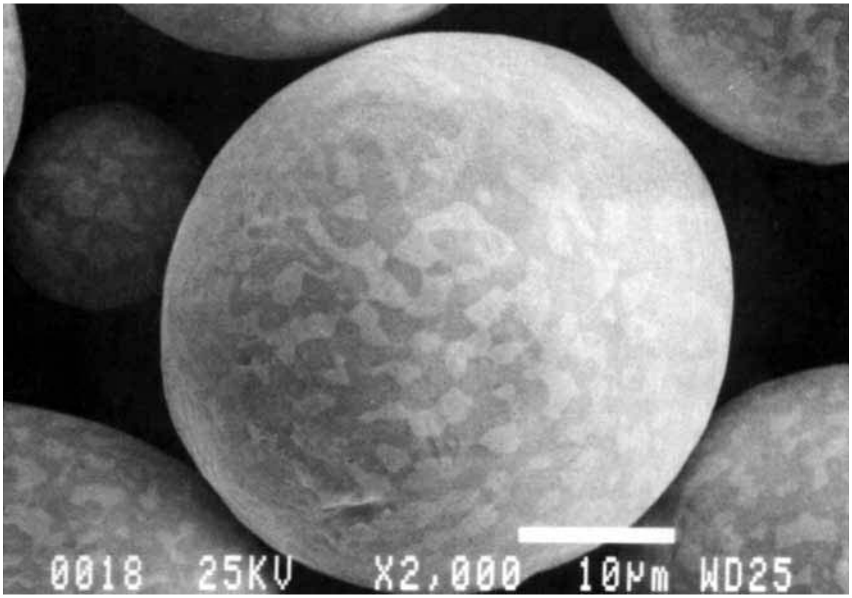


Figure 5.7 SEM micrograph of 63Sn/37Pb powder –325/–500 mesh.

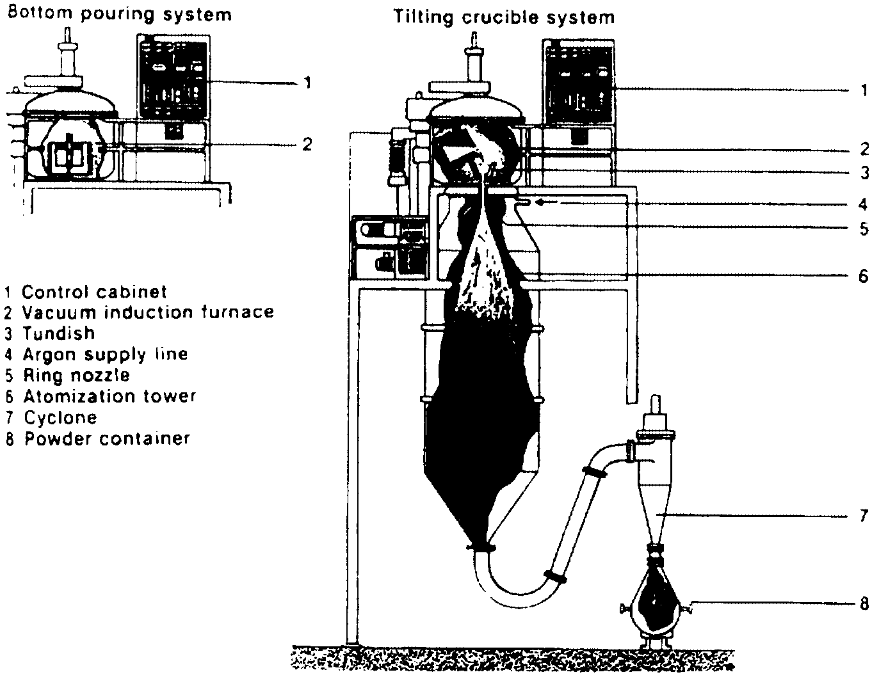


Figure 5.8 Schematic of an inert gas atomization system.

It has been found that the mean volume-surface diameter d is proportional to the surface tension of the atomized liquid and the melting rate but inversely proportional to the angular velocity of the rotating electrode, the diameter of the electrode, and the density of the atomized liquid, expressed by the following relation:

$$d \propto \frac{\gamma^{0.50} Q^{0.02}}{\omega^{1.03} \rho^{0.50} D^{1.05}}$$

where the symbols were defined earlier.[3–5]

The mass proportion of secondary particles P_s is directly related to the angular velocity of the rotating electrode, the density of the atomized liquid, and the melting rate but inversely proportional to the diameter of the electrode and the surface tension of the atomized liquid, expressed by the following relation:

$$P_s \propto \frac{\omega^{0.33} \rho^{0.56} Q^{1.24}}{D^{0.15} \gamma^{1.05}}$$

Metal powder can also be produced by vacuum atomization, which is believed to yield clean and finer particles. For superfine alloy powder, it is reported that a new atomizing technique is available using pulverizing energy produced by a

50-MPa water pump concentrated at the apex of a conical jet by which the thin stream of molten metal is disintegrated into superfine droplets.[6]

Ultrasonic gas atomization is another technique that produces metal powders successfully.[7] A process of two-stage spinning cup atomization with a liquid quenching is in development to produce fine particles with greater latitude in particle-size control.[8]

5.2.4 Mechanical properties

Three fundamental mechanical properties of solders include stress vs. strain behavior, creep resistance, and fatigue resistance.

Although stress can be applied by tension, compression, or shear force, most alloys are weaker in shear than in tension or compression. Shear strength is important, because most solder joints are subjected to shear stress during service.

Creep is a global plastic deformation that results when both temperature and stress (load) are kept constant. This time-dependent deformation can occur at any temperature above absolute zero. However, creep phenomena only become significant at “active” temperatures.

Fatigue is the failure of alloys under alternating stresses. The stress that an alloy can tolerate under cyclic loading is much less than that under static loading. Therefore, the yield strength, a measure of the static stress that solders will resist without permanent deformation, often does not correlate with fatigue resistance. The fatigue crack usually starts as several small cracks that grow under repeated applications of stress, resulting in a reduction of the load-carrying cross section of the solder joint.

Solder in electronic packaging and assembly applications normally undergoes low cycle fatigue (a fatigue life less than 10,000 cycles) and is subjected to high stresses. Thermomechanical fatigue is another test mode used to characterize the behavior of solder. It subjects the material to cyclic temperature extremes, i.e., a thermal fatigue test mode. Either method has its unique features and merit, yet both impose strain cycling on solders.

The ultimate tensile strength, 0.2 and 0.01 percent yield strength, and uniform elongation of common bulk solder alloys are listed in Table 5.3. In the group of Sn/Pb alloys, the strength decreases with decreasing tin content. This trend is expected, with the exception that the eutectic composition does not show the maximum strength. Its origin needs further confirmation.

The 96.5Sn/3.5Ag, 95Sn/5Ag, and 95Sn/5Sb compositions exhibit significantly higher strength and lower elongation. The composition 42Sn/58Bi is particularly strong, yet extremely brittle. In/Sn alloys with high indium content are extremely soft and lack adequate strength. It has been demonstrated that the solder joint strength may not coincide with that of bulk solder alloys because of other external factors, such as solder joint configuration, metallurgical reactions, interfacial wettability, interfacial effect, and the characteristics of other materials incorporated in the assembly.

Figures 5.9 through 5.30 show the creep behavior of solder alloys under a constant load of 920 g (equivalent to 50×10^6 dyn/cm^2 initial stress) at an ambient temperature of 25 ± 3°C.

TABLE 5.3 Tensile Strength and Uniform Elongation of Common Solders

Alloy composition	Liquidus, °C	Solidus, °C	Ultimate tensile strength, 10^3 lb/in^2	0.2% yield strength, 10^3 lb/in^2	0.01% yield strength, 10^3 lb/in^2	Uniform elongation,%
42Sn/58Bi	138	138	9.71	6.03	3.73	1.3
43Sn/43Pb/14Bi	163	144	5.60	3.60	2.77	2.5
30In/70Sn	175	117	4.67	2.54	1.50	2.6
60In/40Sn	122	113	1.10	0.67	0.53	5.5
30In/70Pb	253	240	4.83	3.58	3.08	15.1
60In/40Pb	185	174	4.29	2.89	2.06	10.7
80Sn/20Pb	199	183	6.27	4.30	2.85	0.82
63Sn/37Pb	183	183	5.13	2.34	1.91	1.38
60Sn/40Pb	190	183	4.06	2.06	2.19	5.3
25Sn/75Pb	266	183	3.35	2.06	1.94	8.4
10Sn/90Pb	302	268	3.53	2.02	1.98	18.3
5Sn/95Pb	312	308	3.37	1.93	1.83	26.0
15Sn/82.5Pb/2.5Ag	280	275	3.85	2.40	1.94	12.8
10Sn/88Pb/2Ag	290	268	3.94	2.25	2.02	15.9
5Sn/93.5Pb/1.5Ag	301	296	6.75	3.85	2.40	1.09
1Sn/97.5Pb/1.5Ag	309	309	5.58	4.34	3.36	1.15
96.5Sn/3.5Ag	221	221	8.36	7.08	5.39	0.69
95Sn/5Ag	240	221	8.09	5.86	3.95	0.84
95Sn/5Sb	240	235	8.15	5.53	3.47	1.06
85Sn/10Pb/5Sb	230	188	6.45	3.63	2.62	1.40
5Sn/85Pb/10Sb	255	245	5.57	3.67	2.26	3.50
95Pb/5Sb	295	252	3.72	2.45	1.98	13.70
95Pb/5In	314	292	3.66	2.01	1.79	33.0

Alloys of Sn/Ag, Sn/Sb, and 5Sn/85Pb/10Sb impart high creep resistance, as shown in Figs. 5.9 through 5.12. This is primarily attributed to solution hardening as substantiated by their high strength and low elongation. When load is applied, the deformation is hindered by means of either interaction of solute atoms with dislocations or interaction with the formation and movement of vacancies, resulting in the impediment of the dislocation movement. Figure 5.13 is a creep curve for the composition 85Sn/10Pb/5Sb, exhibiting relatively

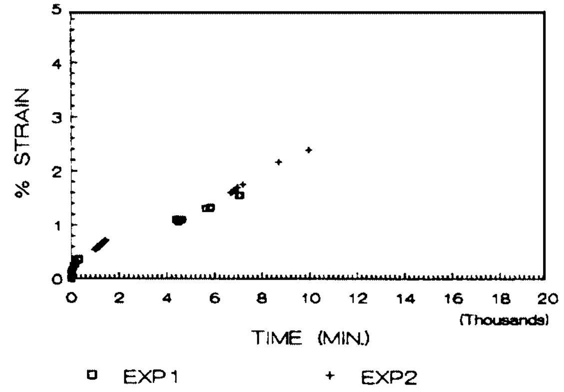


Figure 5.9 Creep curve of 96.5Sn/3.5Ag.

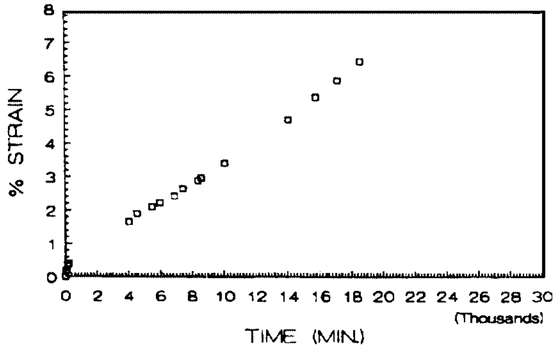


Figure 5.10 Creep curve of 95Sn/5Ag.

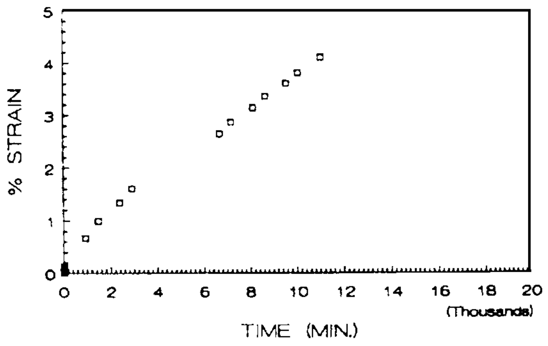


Figure 5.11 Creep curve of 95Sn/5Sb.

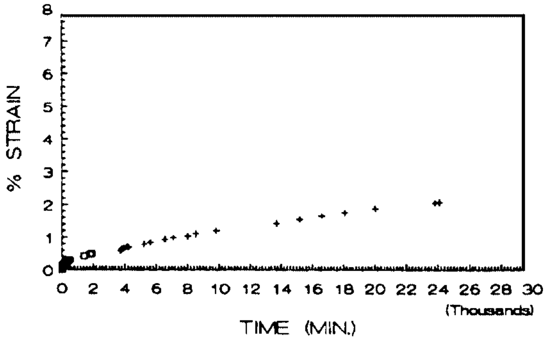


Figure 5.12 Creep curve of 5Sn/85/Pb/10Sb.

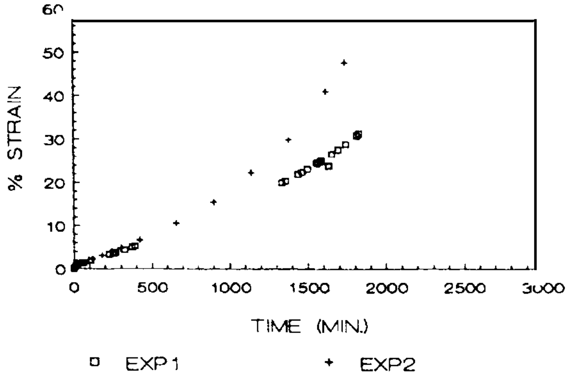


Figure 5.13 Creep curve of 85Sn/10Pb/5Sb.

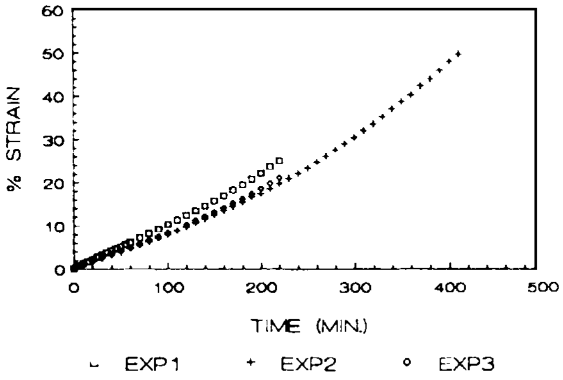


Figure 5.14 Creep curve of 63Sn/37Pb.

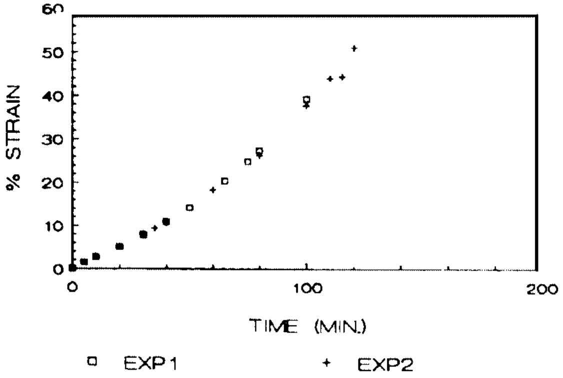


Figure 5.15 Creep curve of 60Sn/40Pb.

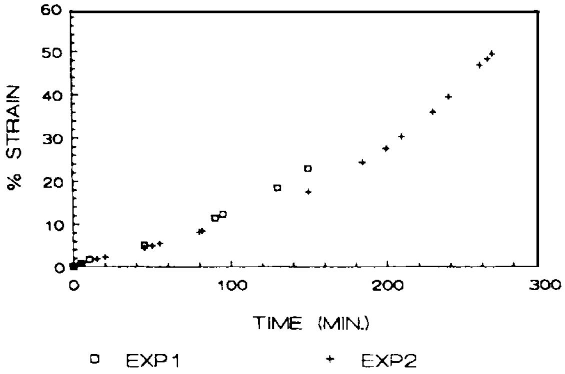


Figure 5.16 Creep curve of 80Sn/20Pb.

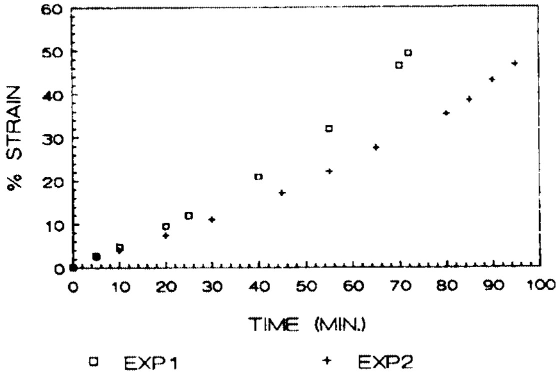


Figure 5.17 Creep curve of 25Sn/75Pb.

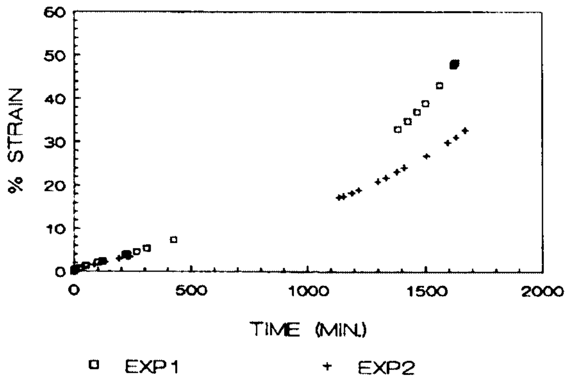


Figure 5.18 Creep curve of 10Sn/90Pb.

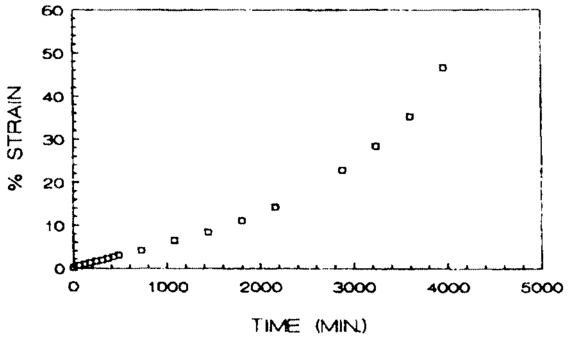


Figure 5.19 Creep curve of 5Sn/95Pb.

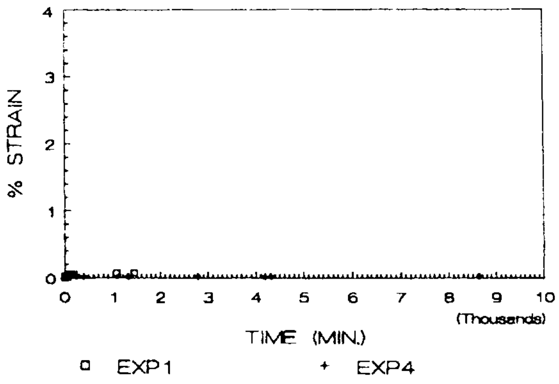


Figure 5.20 Creep curve of 62Sn/36Pb/2Ag.

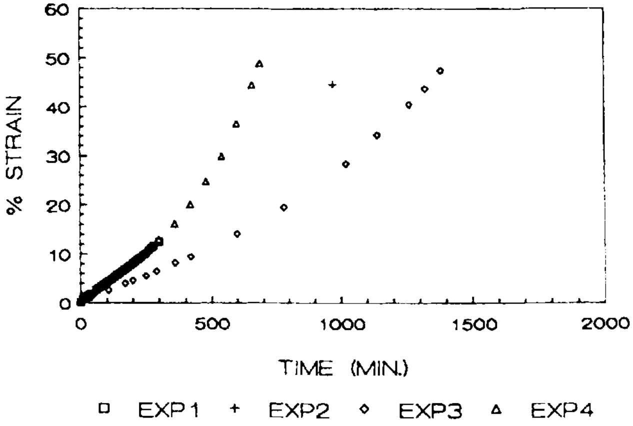


Figure 5.21 Creep curve of 15Sn/82.5Pb/2.5Ag.

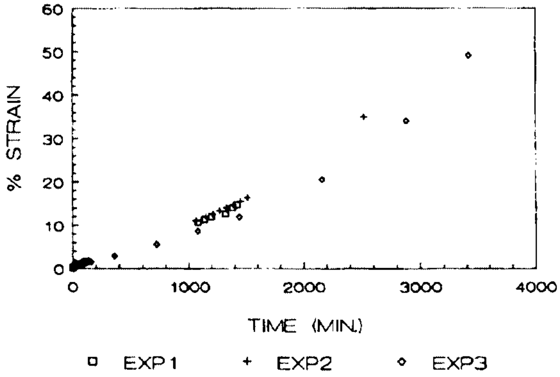


Figure 5.22 Creep curve of 10Sn/88Pb/2Ag.

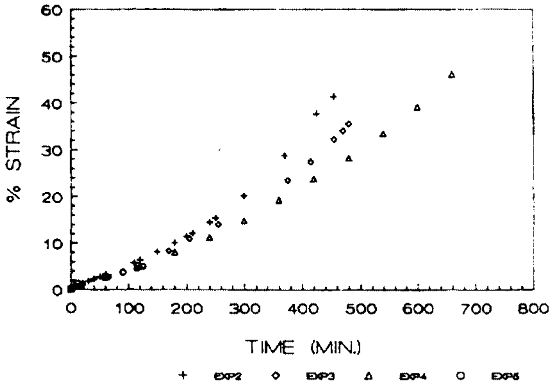


Figure 5.23 Creep curve of 5Sn/93.5Pb/1.5Ag.

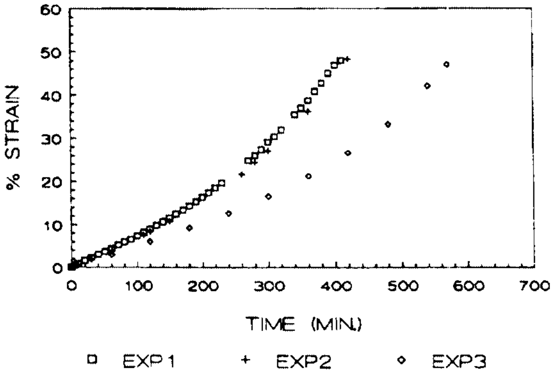


Figure 5.24 Creep curve of 1Sn/97.5Pb/1.5Ag.

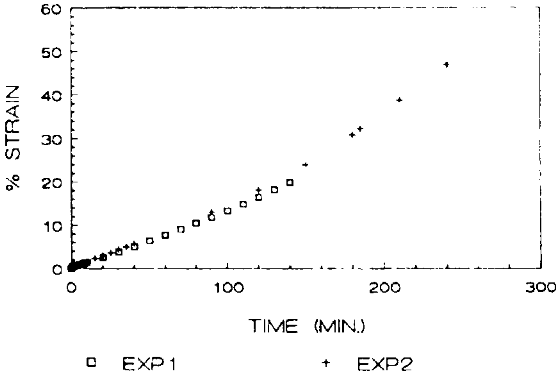


Figure 5.25 Creep curve of 42Sn/58Bi.

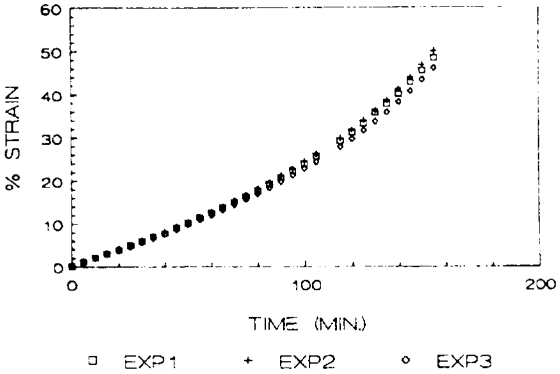


Figure 5.26 Creep curve of 43Sn/43Pb/14Bi.

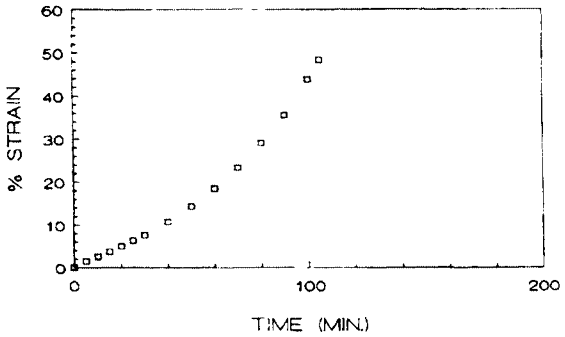


Figure 5.27 Creep curve of 30In/70Sn.

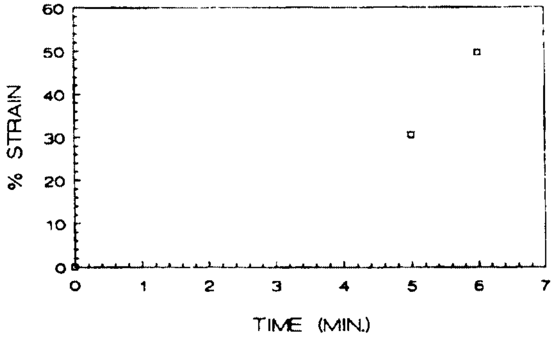


Figure 5.28 Creep curve of 60In/40Sn.

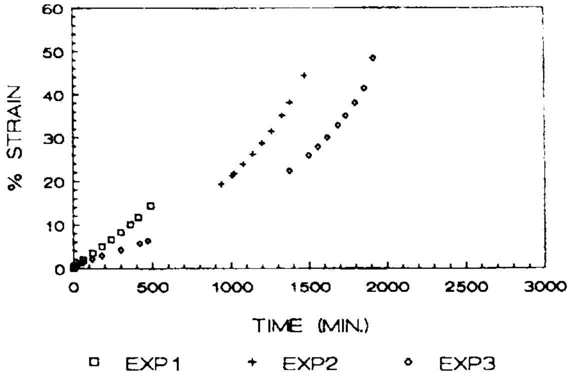


Figure 5.29 Creep curve of 30In/70Pb.

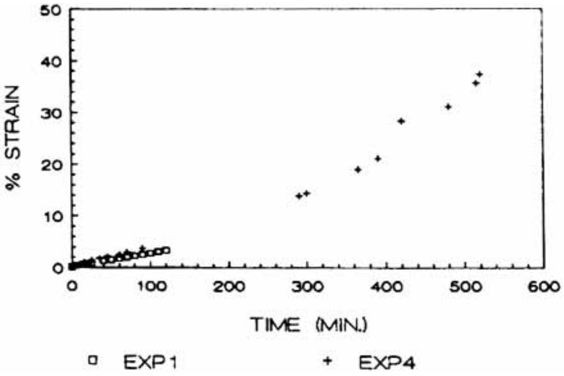


Figure 5.30 Creep curve of 60In/40Pb.

lower creep resistance than 5Sn/85Pb/10Sb. Their melting point may be a factor in creating such a difference.

Figures 5.14 through 5.19 show the creep curves for Sn/Pb compositions. Eutectic 63Sn/37Pb has higher creep resistance than noneutectic compositions 60Sn/40Pb, 80Sn/20Pb, and 25Sn/75Pb. Alloys 10Sn/90Pb and 5Sn/95Pb, however, benefited from the high melting point of their microstructural continuous phase, resulting in the more sluggish steady-state creep, as shown in Figs. 5.18 and 5.19. This is attributed to lower self-diffusion, although the alloys are ductile and have moderate strengths. The creep curves for Sn/Pb/Ag systems are shown in Fig. 5.20 through 5.24. 62Sn/36Pb/2Ag has the highest creep resistance. Its mechanism, whether through the impediment of grain-boundary sliding resulting from silver segregation or the result of high activation energy for the dislocation movement, is not substantiated.

Bismuth alloys, 42Sn/58Bi and 43Sn/43Pb/14Bi, though having high tensile strength, are found prone to creep. This may be primarily a result of their low melting temperatures and the predominance of the diffusion-controlled process. The corresponding creep curves are shown in Figs. 5.25 and 5.26. The In/Sn system has very poor creep resistance, as reflected in Figs. 5.27 and 5.28. The low melting point of their microstructural continuous phase is considered a main factor. While In/Pb compositions are ductile, as shown in the elongation data, the single-phase microstructure and moderate melting points provide moderate creep resistance, as shown in Figs. 5.29 and 5.30.

The creep resistance of the various solder alloys, as shown in Table 5.4, is ranked in five groups—low, low-moderate, moderate, moderate-high, and high. As the testing temperature or the applied load changes, a change in the creep behavior of the alloys may result.

5.3 Solder Paste

Solder paste, by its virtue of deformability and tackiness, is the primary material to make solder connections for surface mount and advanced surface mount processes when it is applied on the mother board (main circuit board)

TABLE 5.4 Relative Creep Resistance of Common Solder Alloys

Alloy composition	Rank	Alloy composition	Rank
42Sn/58Bi	Moderate	5Sn/95Pb	Moderate–high
43Sn/43Pb/14Bi	Low–moderate	62Sn/36Pb/2Ag	High
30In/70Sn	Low	15Sn/82.5Pb/2.5Ag	Moderate
60In/40Sn	Low	10Sn/88Pb2Ag	Moderate–high
30In/70Pb	Moderate	5Sn/93.5Pb/1.5Ag	Moderate
60In/40Pb	Moderate	1Sn/97.5Pb/1.5Ag	Moderate
80Sn/20Pb	Moderate	96.5Sn/3.5Ag	High
63Sn/37Pb	Moderate	95Sn/5Ag	High
60Sn/40Pb	Low	95Sn/5Sb	High
25Sn/75Pb	Low	85Sn/10Pb/5Sb	Moderate
10Sn/90Sb	Moderate	5Sn/85Pb/10Sb	High

and/or when it is used for IC packaging on the module and package level. The deformable form of solder paste makes it applicable in any selected shape and size and readily adaptable to automation; its tacky characteristics provide the capability of holding parts in position without the need of additional adhesives before the permanent bonds are formed.

5.3.1 Definition

Solder paste, by one definition, is a *homogeneous and kinetically stable mixture of solder alloy powder, flux, and vehicle, which is capable of forming metallurgical bonds at a set of soldering conditions and can be readily adapted to automated production in making reliable and consistent solder joints.*

In terms of functionality, a solder paste can be considered as being composed of three major components. These are solder alloy powder, vehicle system, and flux system. The vehicle primarily functions as a carrier for the alloy powder, a compatible matrix for the flux system, and a basis for a desirable rheology. The flux cleans the alloy powder and the substrates to be joined so that high-reliability metallic continuity results and good wetting can be formed. Both vehicle and flux are fugitive or nonfunctional in nature after completion of the soldering. They are nevertheless crucial to the formation of reliable, permanent bonds. On a permanent basis, the alloy powder part is the only functional component in forming a metallurgical bond.

5.3.2 Characteristics

The chemical and physical characteristics of solder paste can be represented by the following parameters:

- Physical appearance
- Stability and shelf life
- Viscosity
- Cold slump
- Dispensability through fine needles
- Screen printability
- Stencil printability
- Tack time
- Adhesion
- Exposure life
- Quality and consistency
- Compatibility with surfaces to be joined
- Flow property before becoming molten
- Wettability
- Dewetting phenomenon
- Solder balling phenomenon
- Bridging phenomenon
- Wicking phenomenon
- Leaching phenomenon
- Quantity and properties of residue
- Residue corrosivity
- Residue cleanability
- Solder-joint appearance
- Solder-joint voids

5.3.3 Fluxes and fluxing[9]

The fundamental key to good solderability lies in ensuring that the surfaces to be joined are “scientifically” clean. Cleanliness must then be maintained during soldering so that a metallic continuity at the interface can be achieved. This cleaning process is called *fluxing*, and the material used is the *flux*.

Customarily, the flux is classified based on its activity and chemical nature, namely rosin-based such as RMA, water-soluble, and no-clean.

Fluxes are applied to the surface to react with metal oxides or nonmetallic compounds, thus “cleaning” them from the metal surfaces. Common metal surfaces that are soldered include Sn/Pb, Sn, Cu, Au, Ag, Pd, Au/Pd, Ag/Pd, Au/Pt, Au/Ni, Pd/Ni, and Ni. Each has its own associated fluxing chemistry.

The flux activity can be determined by the combined measurements in water extract resistivity, copper mirror test, halide test, and surface insulation test.

To achieve fluxing, several approaches are available. Flux can be incorporated into the solder paste or inside the solder wire, it can be applied as a separate chemical directly onto the component and solder paste or inside the solder wire, or it can be applied as a separate chemical directly onto the component and solder pad surface, as with liquid flux used in wave soldering. Still another approach is gas-phase fluxing, which supplies a proper atmosphere to the soldering substrates. Other in-situ cleaning process may render the solder fluxless.

5.3.4 Strength of fluxes

The fluxing strength depends on the intrinsic properties of the flux agent or flux system as well as the external conditions. The factors include the following:

- Functional group and molecular structure of flux agent
- Melting point and boiling point of flux chemicals
- Thermal stability in relation to soldering conditions
- Chemical reactivity in relation to soldering conditions
- Surrounding medium of flux agent
- Substrates to be fluxed
- Environmental stability (temperature, humidity)
- Soldering conditions (temperature versus time, atmosphere)

The effects of molecular structure and medium on the strength of acids and bases are classified as inductive, resonance, hydrogen bonding, solvation, hybridization, and steric effects. For commonly adopted inductive effect, the electronic-withdrawing groups adjacent to the carboxylic group of molecules enhance the acidity strength of the carboxylic group as a result of anion stabilization. Conversely, electron-releasing groups decrease the acidity.

5.3.5 Water-cleaning flux

Water-cleaning flux is designed so that its residue after soldering can be removed by using either pure water or a water medium with the addition of a saponifier or an additive.

Considering performance, process, reliability, and cost, a flux chemistry that requires only water for removal (water-soluble) is the preferred choice. Special notes for using water-soluble solder paste are as follows:

- In the cleaning process, to avoid flux entrapment and incomplete residue removal, ultrasonic cleaning is an effective aid.
- In the soldering process, it is important to control the temperature profile, particularly in terms of peak temperature and dwell time at peak temperature to avoid overheating.

5.3.6 Gas-phase flux

Soldering under controlled-atmosphere conditions has been studied in recent years. Such controlled atmospheres can generally be classified as either *reactive* or *protective*.

The reactive atmosphere can help the fluxing agent clean component leads and solder pads. This approach has strong merits in solderability and leaves minimal residue. However, it should be cautioned that a reactive atmosphere is nonselective. It can react with all materials being exposed as long as the conditions meet thermodynamic and kinetic criteria. Therefore, all materials of an assembly must be compatible with the reactive atmosphere. With the wide variety of materials used in each assembly and the continued incorporation of new components and materials into assemblies, ensuring this compatibility can be quite a task. The protective atmosphere, on the other hand, primarily functions as an oxygen and moisture repellent during soldering without providing external chemical activity. Controlled atmosphere soldering is discussed in Sec. 5.4.6.

5.3.7 No-clean flux

From the user's point of view, no-clean flux (especially incorporated directly into solder paste) requires the following:

- Minimal amount of residue; ideally none
- Residue that is translucent and aesthetically acceptable
- Residue that will not interfere with bed-of-nails testing
- Residue that will not interfere with conformal coating where applicable
- Residue that is nontacky
- Residue that stays inert under exposure to temperature, humidity, and voltage bias
- Ability to flux effectively without solder-ball formation

Because of the wide variety of design and performance requirements in board assemblies, the acceptable amount of residue and the physical and chemical properties of the residue will vary from one application to another. An application-specific approach is needed. Success with a no-clean product requires close communication and collaboration between user and supplier to design a best-fit flux (material) and fluxing (process) system.

Common solder paste tests in chemical and physical characteristics continue to apply to no-clean systems. The industry's established test parameters and methods can be used to assess the quality and properties of the assemblies. These include ionic contaminant test and visual examination. However, the tests for no-clean system have one difference. These tests should be conducted after reflow or soldering. The solder paste chemical makeup measurement in terms of ionic mobility must be also taken after exposure to a specified reflow condition, not before exposure. This procedure is designed to target the characteristics of the residue left on the board, not the as-is paste chemistry.

5.3.8 Comparison between water-clean and no-clean

With proper cleaning process and reflow parameters, a water-soluble process can produce clean assemblies in both function and appearance. In addition, the nature of its chemistry imparts wider fluxing latitude, better accommodating the inherent variations in solderability of components and boards. It requires initial equipment capital, added operating costs in energy and water consumption, and expenditures on consumables for a closed-loop recycle system.

No-clean (air) systems eliminate one process step, which is clearly an economic advantage. It should be noted that the cleaning process has been perceived as a step to remove residues from solder flux or paste, yet it actually has provided the cleaning function for components and boards for many operations without being noticed. It is not unusual for boards, before fluxing and soldering, to contain higher amounts of ionic contaminants than after soldering and cleaning. The level of as-received contamination may exceed the acceptable level, because most steps in board fabrication and component plating involve highly ionic chemicals.

For a no-clean system that requires soldering under a protective atmosphere such as N_2, the cost of N_2 may offset or exceed the savings gained from no-clean operations, depending on N_2 consumption and the unit cost of N_2, which varies with the location. Other factors that may also complicate the assessment of a no-clean system are solder ball effect and the acceptability of residue appearance.

Nonetheless, both water-clean and no-clean routes are viable application systems. A basic understanding of the principles behind each practice and the compliance with application requirements is essential to the success of implementing either manufacturing system. Table 5.5 summarizes the general feature comparison between water-clean and no-clean, and Table 5.6 illustrates viscosity and metal load of despensing and printing pastes.

TABLE 5.5 Comparison of Water-Soluble vs. No-Clean (Air)

	Water-soluble	No-clean (air)
Merits	• Clean assembly in function and appearance • Latitude for solderability variation	• One less process step • Lower operating and capital expenses
Drawbacks	• Extra step of process-cleaning • Operating cost—water, energy, and consumables • Initial capital expenditure	• Unable to remove contaminants from board and components • Often demand higher level of process control • Uncertainty in solder ball effect • Appearance issue • Possible limits for high-frequency application and/or uses that demand extraordinary extension of fatigue

TABLE 5.6 Viscosity and Metal Load of Dispensing and Printing Pastes

Solder paste type	Viscosity, cP*	Metal load, wt%
Fine dot dispensing	200,000–450,000	To 88
Screen printing	450,000–1,000,000	To 92
Stencil printing	700,000–1,600,000	To 92

*Centipoise, Brookfield RVT viscometer, TF/5 r/min, 3-min mixing/2-min reading.

5.3.9 Rheology

Paste applicability depends on its rheology, that is, its flow and deformation behavior. The primary driving forces underlying the rheology of solder paste include both kinetic and thermodynamic contributions. Therefore, the rheology of solder paste may be affected by the following factors:

- Composition, shape, and size of suspended particles
- Chemical composition of suspending matrix
- Relative concentration of effective ingredients in matrix
- Structure of ingredients in matrix
- Interactions between matrix and suspended particles either physical or chemical in nature, including wetting and solvation
- Volume fraction occupied by suspended particles—usually, the higher the amount of particles, the more deviation from viscous flow
- Internal structure and its response to external forces
- Interactions among particles and resulting aggregates and flocculants
- Temperature

The difficulty of predicting the rheology of such a system is apparent and a result a lack of knowledge of the detailed structure and the nature of forces exerted by molecules or particles. However, its behavior can be characterized. It is also apparent that solder paste is not an elastic material, nor is it a pure viscous material. Viscoelasticity best describes the behavior of solder paste. The characterization of viscoelasticity and fundamental theories are covered in the literature.[1,10]

The common methods used to transfer solder paste consistently and accurately onto the intended solder pads include mesh screen printing, metal mask stencil printing, pneumatic dot and line dispensing, and positive displacement dispensing. Figures 5.31 and 5.32 illustrate the flow behavior of a dispensing paste and a printing paste, respectively.[1] The paste possessing a low yield point and very slight plastic behavior is found most suitable for dispensing applications, and a moderate yield point and thixotropy are generally associated with the printing paste. Table 5.6 lists typical viscosity and metal load percentages for dispensing and printing application techniques.

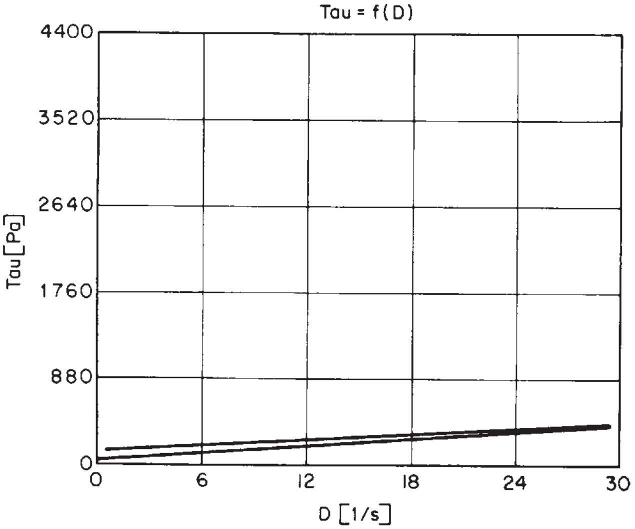


Figure 5.31 Flow curve of dispensing paste.

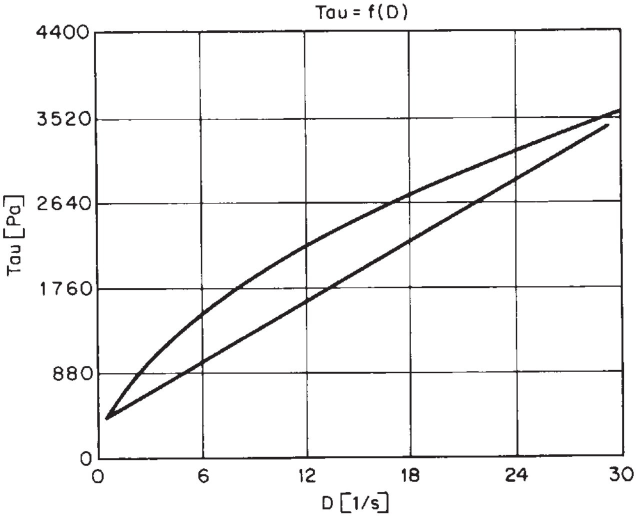


Figure 5.32 Flow curve of printing paste.

The size distribution of particles suitable for solder paste ranges from 45 to 74 µm in diameter, corresponding to –200/+325 mesh, are compatible with the printing standard of 0.050- to 0.25-in pitch land patterns, as well as with dispensing up to 20 gauge. For finer-pitch applications, smaller than 0.025-in pitch or 20 gauge, solder powder smaller than 45 µm in diameter is needed.[11]

The printing thickness is another factor. Although the thicker paste deposit may impart a "better" joint, the maximum paste thickness for 0.050-, 0.025-, and 0.012-in pitch land patterns are generally limited to 0.015, 0.008, and 0.004 in, respectively.

5.3.10 Formulation

As an example, a typical RMA solder-paste formula may contain 10 to 15 ingredients that provide various intended functions as shown in Table 5.7. The formula may appear to be straightforward. However, designing a viable product capable of delivering all the desired performance characteristics is complex and requires understanding the technologies.

TABLE 5.7 Ingredients of Typical RMA Solder Paste

Ingredient	Function
Rosin	Rosin system for designated softening point, acid number, thermal stability, fluxing activation, tackiness
Nonhalogen activator	Activator system for accomplishing fluxing action over a wide range of temperatures, rheology
Solvent	Solvent system to accommodate solubility, rheology, temperature compatibility, chemical compatibility
Binder	Providing compatible viscosity, rheology, tackiness
Fluxing modifier	Stabilizing and modifying flux
Rheology modifier	Contributing to targeted rheology

The following thinking steps are one route to take in developing a product:

1. Define performance objective.
2. Utilize fundamental technologies.
3. Select raw materials.
4. Understand and anticipate potential synergistic or antagonistic interactions between ingredients.
5. Balance performance parameters.
6. Fine-tune the formula to meet designated specifications.
7. Develop production process.
8. Produce consistent product.

A product involves many performance parameters, and some of them are trade-offs. For example, a high metal content is beneficial to solder joint volume and reduced voids and residue, yet it makes the paste more prone to drying and difficult to apply. A high-viscosity paste may improve flow control against temperature, but it causes the paste to be difficult to apply. Using highly active fluxing chemicals may improve solderability in some cases, but their use may leave a more corrosive residue. In such cases, improving the solderability by selecting the proper ingredients without the use of highly active fluxing chemicals is the essence of technology. It should be noted that increasing the flux content does not always improve solderability in terms of wetting or the elimination of solder balling.

After the product has been designed, developing a reproducible process for making the paste with consistent characteristics is equally important. It is not an exaggeration, but an indication of the importance of the role of the process, to state that the identical composition formula can produce different results when the process is allowed to vary.

The design of water-soluble and no-clean products follows the same principle, but specific chemical ingredients differ.

5.3.11 Design and use of solder paste for system reliability

With the versatility of components and the vast variation in their solderability, it is tempting to formulate a flux chemistry with high activity. It is also convenient to incorporate the halide-containing organic ingredients to enhance the activity without adversely affecting the test results in the content of ionic species. This is because organic halides can be very effective fluxing agents in a very low dosage, thus relieving the level of elaboration (skills) in formulation technology. In addition, in various chemical makeups, low-dosage halides may be able to pass the “standard” tests. It is a well established fact that, among the chemical families, mobile halides are the most reactive species toward metals that make up the circuitry. Thus, their use should be discouraged.

Finer powder obviously facilitates the fine-pitch deposition via printing or dispensing. Undesirably, the paste with finer powder results in higher demand in the content, as well as in the activity of flux, and is more often prone to solder balling during reflow. Finer powder is also associated with higher cost.

Thus, it is always advantageous to use the coarsest powder that is allowable by a flux/vehicle system for achieving the printability and dispensability so that the reduced cost and proper flux activity can be obtained.

As the large or heavy array packages are incorporated in the assembly, the disparity of heat transfer is heightened. In those cases, increasing the temperature has indeed accommodated most reflow results. However, from a reliability standpoint, the approach may not be sound when considering the advent of heat-sensitive components, more complex PCB design, and increasingly versatile components contained in an assembly.

Reflow profiles based on slower heating and cooler temperature will be more in sync with today’s complex assemblies, minimizing in-process heat-induced damage as well as the level of residual stress, which may cause problems such as PBGA package cracking, board warpage, and board delamination. These three areas affect not only the production floor first-pass defect rate and yield but also the long-term performance of the assembly.

The principles of design and use of solder paste—mild flux, coarse powder, and low-temperature reflow profile—work in tandem, toward achieving the highest system reliability.

5.3.12 Quality assurance tests

Tests to assure the properties and performance of a solder paste can be grouped into five parts: paste, vehicle, powder, reflow, and post reflow. Table 5.8 summarizes the tests in each of the five parts.[1]

5.4 Soldering Methodology

5.4.1 Types

The commercially available reflow methods include conduction, infrared, vapor phase, hot gas, convection, induction, resistance, and laser. Each of these reflow methods has its unique features and merits in cost, performance, or operational convenience. For localized and fast heating, laser excels over other methods, with hot air in second place. For uniformity of temperature, vapor phase ranks first. For versatility, volume, and economy, convection and infrared are the choices. Conduction heating, however, is a convenience for low-volume and hybrid assembly. For conductive components requiring fast heating and high-temperature soldering, induction heating meets the requirement. Table 5.9 summarizes the strength and limitations of each method.

5.4.2 Reactions and interactions

During soldering, a series of reactions and interactions occur in sequence or in parallel. These can be chemical or physical in nature in conjunction with heat transfer. The mechanism behind fluxing is often viewed as the reduction of metal oxides. Yet, in many situations, chemical erosion and dissolution of oxides and other foreign elements act as the primary fluxing mechanisms. Using a more complex fluxing process in solder paste as an example, the primary steps are represented by the flowchart in Fig. 5.33.

5.4.3 Process parameters

With the prevalence of infrared and convection reflow, a few more words about furnace profile and furnace operating parameters are pertinent. It should be stressed that the reflow is a dynamic heating process in that the condition of the workpiece is constantly changing as it travels through the furnace in a relatively short reflow time. The momentary temperature that the workpiece experiences determines the reflow condition; therefore, the reflow results.

It is ultimately important to establish a correlation between the set temperature of a given furnace, the measured temperature of the workpiece at each specified belt speed, and the soldering performance. The resulting correlation between soldering performance and temperature setting or profile provides a "workable range" for the assembly.

TABLE 5.8 Summary of Quality Assurance Tests for Solder Paste

Paste
Appearance
Metal content and flux-vehicle percentage
Density
Viscosity
Viscosity versus shear rate
Cold slump
Hot slump
Molten flow
Tack time
Dryability
Dispensability
Printability
Shelf stability
Storage, handling, and safety
Flux/vehicle
Water extract resistivity
Copper mirror corrosion
Chloride and bromide
Acid Number
Infrared spectrum fingerprint and other spectroscopies
Solder powder
Alloy composition
Particle size, sieve
Particle size distribution, sedigraph
Particle shape
Particle surface condition
Dross
Melting range
Reflow
Solder ball
Solderability
Exposure time
Soldering dynamics
Post reflow
Cleanliness, resistivity of solvent extract
Surface insulation resistance, before and after cleaning
Solder joint appearance
Solder voids
Joint strength
Power cycling
Temperature cycling
Vibration test
Simulated aging
Thermal shock

Under mass reflow operation, both heating and cooling steps are important to the end results. It is generally understood that the heating and cooling rates of reflow or soldering process essentially contribute to the compositional fluctuation of the solder joint. This is particularly true when there are significant levels of metallurgical reactions occurring between the Sn/Pb solder and substrate metals. In the meantime, the cooling rate is expected to be responsible for the evolution of the microstructure.

TABLE 5.9 Outline of Benefits and Limitations of Reflow Methods

Reflow method	Benefits	Limitations
Conduction	Low equipment capital, rapid temperature changeover, visibility during reflow	Planar surface and single-side attachment requirement, limited surface area
Infrared	High throughput, versatile temperature profiling and processing parameters, easier zone separation	Mass, geometry dependence
Vapor phase condensation	Uniform temperature, geometry independence, high throughput, consistent reflow profile	Difficult to change temperature, temperature limitation, relatively high operating cost
Hot gas	Low cost, fast heating rate, localized heating	Temperature control, low throughput
Convection	High throughput, versatility	Slower heating, higher demand for flux activity
Induction	Fast heating rate, high temperature capacity	Applicability to nonmagnetic metal parts only
Laser	Localized heating with high intensity, short reflow time, superior solder joint, package crack prevention	High equipment capital, specialized paste requirement, limit in mass soldering
Focused infrared	Localized heating, suitable for rework and repair	Sequential heating, limit in mass soldering
White beam	Localized heating, suitable for rework and repair	Sequential heating, limit in mass soldering
Vertical reflow	Floor space saving, maintenance of desired throughput	Often more costly

The key process parameters that affect the production yield as well as the integrity of solder joints include the following:

- Preheating temperature
- Preheating time
- Peak temperature
- Dwell time at peak temperature
- Cooling rate

It should be stressed that the reflow in a furnace (infrared or convection) is a dynamic heating process in that the conditions of the workpiece are constantly changing as it travels through the furnace in a relatively short reflow time. The momentary temperature that the workpiece experiences determines the reflow conditions and therefore the reflow result.

Figure 5.34 illustrates a simulated reflow profile comprising three stages of heating:

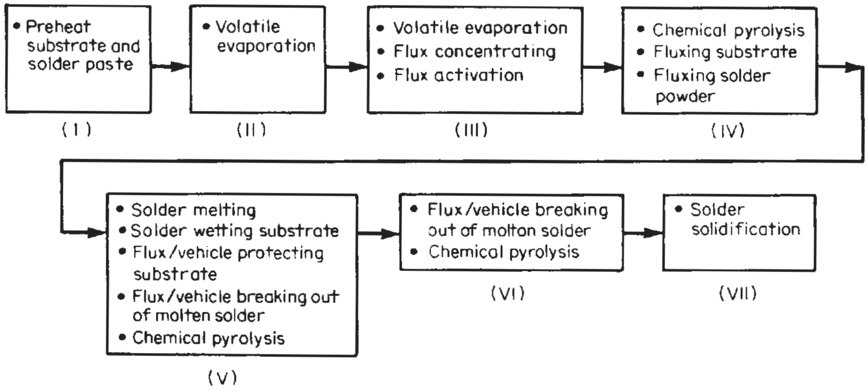


Figure 5.33 Flow chart of reflow dynamics.

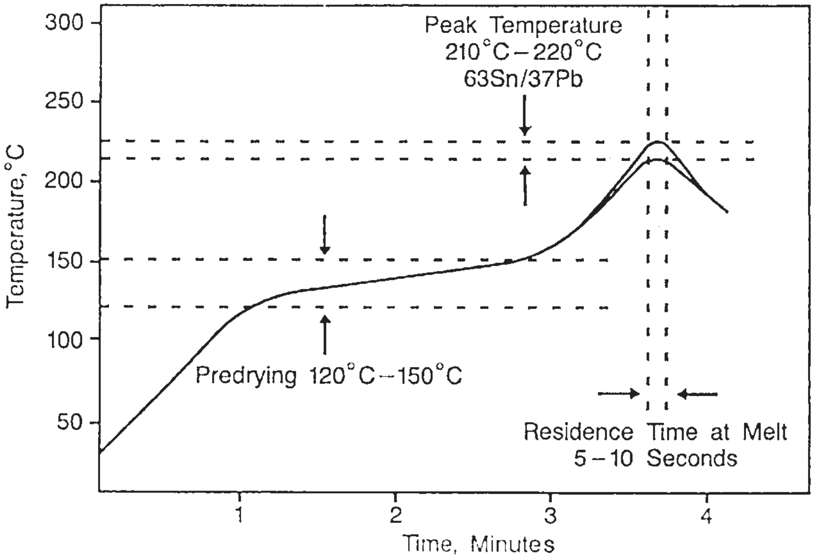


Figure 5.34 Reflow profile comprising three stages of heating.

1. Natural warm-up
2. Preheating/soaking
3. Spike and reflow

In the natural heating stage, the heating rate of reflow profiles being used in the industry falls in the range of 2 to 4°C. The parameters of the preheating/soaking stage are important to the reflow results. The desirable preheating rate is less than 1°C/s. During soldering dynamics, the heating process contributes not only to the effectiveness of wetting but also to the extent of metallurgical reactions between solder and the substrates to which the solder interfaces, particularly the peak temperature and the dwell time at the temperature above the liquidus of the solder.

Several events occur during this stage, as shown in steps (2) and (4) of the flow chart (Fig. 5.33). These include temperature set to fit the specific flux activation temperature of the chemical system of the paste and the time at heat to fit the constitutional makeup of the paste. Inadequate preheating often causes a spattering problem that manifests itself as discrete solder balls. Too high a temperature or too long a time at the elevated temperature can result in insufficient fluxing and/or overdecomposition of organic, causing solder balling or hard-to-clean residue (if the no-clean route is adopted). The recommended general conditions for the second stage are 120 to 150°C for a duration of 45 to 150 sec. The third stage is to spike quickly to the peak reflow temperature at a rate of 1.0 to 4.0°C/s. The purpose of temperature spiking is to minimize the exposure time of the organic system to high temperature, thus avoiding charring or overheating. Another important characteristic is the dwell time at the peak temperature. The rule of thumb in setting the peak temperature is 20 to 50°C above the liquidus or melting temperature; e.g., for the eutectic Sn/Pb composition, the range of peak temperatures is 203 to 233°C.

The wetting ability is directly related to the dwell time at the specific temperature in the proper temperature range and to the specific temperature being set. Other conditions being equal, the longer the dwell time, the more wetting is expected—but only to a certain extent; the same trend applies at higher temperatures. However, as the peak temperature increases or the dwell time is prolonged, the extent of the formation of intermetallic compounds also increases. An excessive amount of intermetallics can be detrimental to long-term solder-joint integrity. Peak temperature and dwell time should be set to reach a balance between good wetting and to expel any nonsolder (organics) ingredients from the molten solder before it solidifies, thus minimizing void formation.

For a given system, the cooling rate is directly associated with the resulting microstructure, which in turn affects the mechanical behavior of solder joints.[2]

It was found that the microstructural variation and corresponding failure mechanisms of solder joints that were made under various reflow temperature profiles are extremely complex. Nonetheless, some correlation between the cooling rate and the basic properties can be obtained.

The copper/solder/copper system is a good example, because it is still the most common material combination electronics assemblies. In this system, 63 Sn/37Pb solder joins copper pads (coated or uncoated) on the printed circuit board with the Sn/Pb coated copper leads of IC components.

For the tinned Cu-63Sn/37Pb-tinned Cu assembly, the reflowed solder joints are cooled in five different manners that deliver four cooling rates—0.1°C/sec, 1.0°C/sec, 50°C/sec, and 230°C/sec, respectively, as measured above 100°C. The fifth cooling mode was conducted in a two-step cooling, resulting an uneven cooling with an average cooling rate of 12°C/sec. Each of the five cooling modes produced a different development of microstructure of solder joint.[2]

5.4.4 Reflow temperature profile

The reflow temperature profile, representing the relationship of temperature and time during the reflow process, depends not only on the parameter settings but also on the capability and flexibility of equipment. Specifically, the instantaneous temperature conditions that a workpiece experiences are determined by

- Temperature settings to all zone controllers
- Ambient temperature
- Mass per board
- Total mass in the heating chamber (load)
- Efficiency of heat supply and heat transfer

For furnace-type reflow process, two profiles are taken to illustrate the effect of temperature profile on the reflow results.

Figures 5.35 and 5.36 show the actual temperature profiles of a convection oven, first with a relatively lower preheat temperature, as shown in Fig. 5.35, and then a higher preheat temperature, as shown in Fig. 5.36. The importance of the compatibility of solder paste chemistry and the assembly system with the reflow temperature profile can be easily demonstrated. For instance, if the solder paste and the assembly require the temperature profile of Fig. 5.35, performing reflow under the temperature profile of Fig. 5.36 may give rise to the following phenomena:

- Deficiency of flux, resulting in solder balls
- Overheating of organics, resulting in cleaning difficulty for processes that are designed to include a cleaning step

On the other hand, if the paste is designed for the higher preheat temperature and/or assembly requires additional heat, using the lower preheat temperature profile can produce the following phenomena:

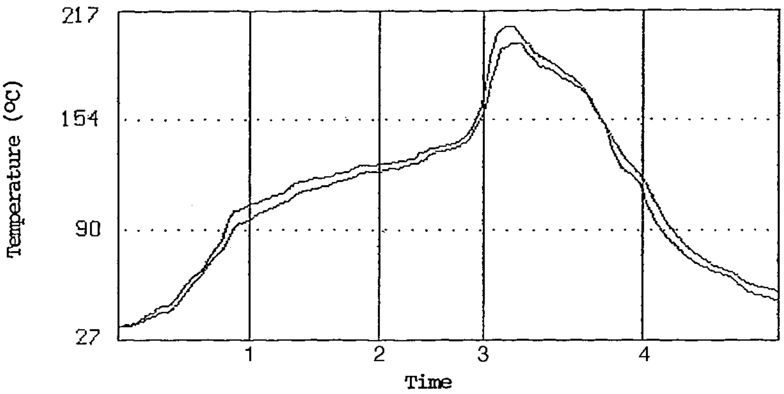


Figure 5.35 Convection reflow profile with lower-temperature preheating.

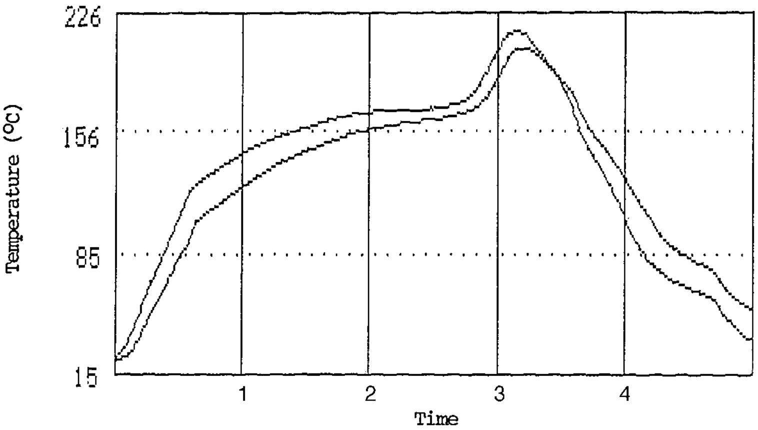


Figure 5.36 Convection reflow profile with higher-temperature preheating.

- Uneven soldering, resulting in cold solder joints
- An excessive amount of residue remaining or non-dry residue from no-clean paste

The temperature profile with boosted preheating conditions, as shown in Fig. 5.36 is most useful for the assembly that is densely populated with components with a large disparity in mass.

Depending on the type of conveyorized furnace, the mass of the assembly and the degree of loading, the major operating parameters to be monitored for effective reflow are the belt speed and the temperature settings of individual zones. The relationship between temperature settings and belt speed; increasing belt speed decreases the resulting peak temperature while other conditions are equal, as shown in Fig. 5.37. Because the required peak temperature is set at 20 to 50°C above the melting temperature of a solder alloy, the working range of peak temperature is always fixed. For every temperature profile, a relationship between peak temperature and belt speed can be

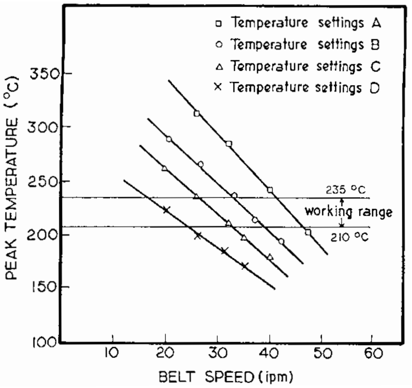


Figure 5.37 Reflow oven belt speed vs. peak temperature.

established, and usable range of belt speeds as depicted in Fig. 5.37 can be obtained.

5.4.5 Effects of reflow profile

The reflow profile used for surface mount manufacturing has a direct bearing on manufacturing yield, solder-joint integrity, and the reliability of the assembly. Specific areas that are affected by reflow profile are listed below. Each area may be affected, to a different degree, by one or more of the three heating stages.

- Temperature distribution across the assembly
- Plastic IC package cracking
- Solder balling
- Solder beading
- Wetting ability
- Residue cleanability
- Residue appearance and characteristics
- Solder joint voids
- Metallurgical reaction between solder and substrate surface
- Microstructure of solder joints
- Board warpage
- Residual stress level of the assembly

5.4.5.1 Uniformity of temperature distribution. In a normal reflow environment, temperature differential across the assembly is inevitable. This results from the large disparity in mass and in the characteristics of the components coupled with the relatively short total reflow time (the entire cycle lasts only several minutes). A large temperature differential causes uneven soldering, resulting in localized cold joints or overheated joints. These problematic joints may contribute to manufacturing defects or jeopardize the long-term integrity of the solder joints under service conditions if they are not detected as manufacturing defects and corrected.

For a given oven, the rate of natural warm-up (in °C/sec) and the intended preheat temperature and time are the main factors that control temperature uniformity across the assembly. A slower heating rate in the warm-up state is desired to reach a more uniform board temperature distribution.

5.4.5.2 Plastic IC package cracking. Along with factors such as die size, the moisture sensitivity of the molding compound, and its thickness, reflow profile plays an important role in causing or preventing plastic IC package cracks. When the IC package (e.g., BGA, QFP, SOIC) absorbs a certain level of moisture during storage, handling, or transit (without proper dry pack), the absorbed moisture may cause package cracking during reflow. Setting a proper reflow profile can mitigate the cracking problem; the heating rate from ambient temperature to 140 to 150°C is most critical.[2]

5.4.5.3 Solder balling. Elevated temperatures and excessive time at those temperatures during the warm-up and preheating stages can result in inadequate fluxing activity or insufficient protection of solder spheres in the paste, causing solder balling. In addition to the quality of solder paste, the presence of solder balls may be essentially related to the compatibility between the paste and the reflow profile. On the other hand, inadequate preheating or heating too fast may cause spattering, as evidenced by random solder balls. The two heating stages preceding the spike/reflow zone are primarily responsible for this phenomenon.

5.4.5.4 Solder beading. Solder beading refers to the occurrence of large solder balls (usually larger than 0.005 in [0.13 mm] in diameter) that are always associated with small and low-clearance passive components (capacitors and resistors). This problem will occur even when the paste may otherwise perform perfectly, i.e., free of solder balls at all other locations (components) on the board and with good wetting. The trouble with solder beading is that it may occur in most or all board assemblies, rendering the first-time yield to nearly zero. The current remedy on the production floor is to manually remove the beads.

The formation of solder beads near or under capacitors and resistors is largely attributed to paste flow into the underside of the component body between two terminations aided by capillary effect. As this portion of paste melts during reflow, it becomes isolated away from the main solder on the wettable solder pads, forming large discrete solder beads. With other factors, reflow profile is a contributor to this phenomenon The practice of adopting a slower preheating rate and a lower reflow peak temperature can reduce solder beading. However, if the reflow profile is at its optimum, and the problem still persists, a new paste with a strengthened chemistry is the solution.

5.4.5.5 Wettability. The temperature setting and time spent in both preheating and spike/reflow affect wettability. However, each stage works by a separate mechanism. In the preheating stage, the range of temperature and the time spent in this range directly affect the activity of flux. Wettability, in turn, is affected by the fluxing action. However, in the spike/reflow zone, wetting on the “cleaned” surface is influenced by the peak temperature because of the intrinsic wetting ability of molten solder alloy. This ability increases on a wettable substrate with higher temperature. With all other conditions being equal, a longer dwell time can, to a limited degree, further enhance wetting. Modification of the spike/reflow zone may sometimes solve a minor wetting problem.

5.4.5.6 Cleanability. In the case of solder paste that is designed to be cleaned, particularly water cleaned, excessive heat may make it difficult for the residue to be removed, rendering a normal cleaning process ineffective. In this case, all stages of the reflow profile can be contributors.

5.4.5.7 Residue appearance and characteristics. The importance of the compatibility of the solder paste's chemical composition with the reflow profile can be readily demonstrated when using a no-clean soldering process. For instance, if the paste is reflowed with a temperature profile below the heat requirement, a higher amount of residue than expected will remain. In addition, the characteristics of that residue may range from being tacky to ionically active.

5.4.5.8 Solder joint voids. Incomplete outgassing (gases entrapped in the solder joint) is the main cause of voiding. In addition to design factors, the compatibility between the reflow profile and the chemical makeup of solder paste is important. There should also be sufficient dwell time in the molten state (above 183°C for 63Sn/37Pb) to ensure that the gases have enough time to separate and escape from the molten solder.

5.4.6 Optimal profile

The heat transfer from the surrounding hot air to the various components on the board, such as leaded packages, array packages, and discretes, differs during the process such that a thermal equilibrium hardly exists. This disparity can be compensated for by either setting a reflow profile with a higher heat supply rate and higher temperature or one with a slower heating rate and lower temperature. On most manufacturing lines, unfortunately, a reflow profile with a higher heating rate and higher temperature is often used.

This disparity in the heat transfer may be heightened as large or heavy array packages are incorporated. Although increasing the temperature has accommodated most reflow results, the approach will not work well with heat-sensitive elements or with PCBs that contain increasingly versatile components.

The initial warm-up state plays a far more influential role in the quality and reliability of assembled boards than was first thought. An initial heating rate at less than 1°C/sec in conjunction with the heating rate for the rest of profile at not more than 3°C/sec is considered most beneficial and is recommended. Under SMT environments, the small degree of reduction in heating rate would not be a bottleneck for production throughput. By using the slower rate in the warm-up and preheating stages prior to reaching 183°C, the peak temperature can be maintained in the range of 210 to 215°C, in contrast to 215 to 230°C. The total dwell time above the liquidus temperature (183°C) falls in the range of 30 to 65 sec.

Reflow profiles bases on slower heating rates and cooler temperatures will be more in line with today's complex assemblies, minimizing in-process heat exposure as well as residual stress.

5.4.7 Laser soldering[1]

Two types of laser have been applied to solder reflow—carbon dioxide (CO_2) and neodymium-doped yttrium-aluminum-garnet (Nd:YAG). Both generate radiation in the infrared region with wavelengths of about 10.6 μm from the CO_2 laser and 1.06 μm for the YAG laser. The wavelength of 1.06 μm is more effectively absorbed by metal than by ceramics and plastics; the wavelength of 10.6 μm is normally reflected by conductive surfaces (metals) and absorbed by organics.

The main attributes of laser soldering are short-duration heating and high-intensity radiation, which can be focused onto a spot as small as 0.002 in (0.050 mm) in diameter. With these inherent attributes, laser reflow is expected to

- Provide highly localized heat to prevent damage to heat-sensitive components and to prevent cracking of plastic IC packages
- Provide highly localized heat to serve as the second or third reflow tool for assemblies demanding multiple-step reflow
- Require short reflow time
- Minimize intermetallic compound formation
- Minimize leaching problems
- Generate fine-grain structure of solder
- Reduce stress buildup in solder joint
- Minimize undesirable voids in solder joint

With these attributes in mind, laser soldering is particularly beneficial to soldering densely packed regions, where local solder joints can be made without affecting the adjacent parts, to soldering surface-mount devices on printed-circuit boards having heat sinks or heat pipes, and to soldering multilayer boards. In addition, it also provides sequential flexibility of soldering different components and enhances the high-temperature performance of adhesives used for mounting surface-mount devices.

With respect to reflow time, laser soldering can be accomplished in less than 1 sec, normally in the range of 10 to 800 ms. The laser can be applied to point-to-point connections through pulsation as well as to line-to-line connections via continuous laser beam scan.

The fine-pitch flat-pack devices have been connected to printed wiring boards using YAG continuous laser beam scans on each side of the package. Both the use of prebumped solder pads and the direct application of solder paste are feasible. In directly reflowing solder paste, although using spattering and heat absorption problems have been observed, they are not incurable. To eliminate these problems, the preheating and predrying step is necessary. Location of laser beam imprringement is another factor. In addition, compatible properties of solder paste have be designed to accommodate fast heating in relation to fluxing and paste consistency, coupled with the proper design of the equipment and its settings.

In using the laser, another concern is energy absorption by the printed-circuit boards, which leads to board damage. This is considered to have been corrected by switching from CO2 laser to YAG laser. Due to the wavelength difference, the energy absorption by polymers can be minimized. Lish[11] has found that sometimes complications may occur. In assembling multilayer polyimide boards by using laser as a second-step reflow, burning was found in the board while it was moving under the laser. The burning was traced to the color pigments contained in the adhesive, which was used for attaching heat sinks. The problem was eliminated by using colorless pigment in the adhesive. This is another clear demonstration that a consideration of all materials in the reflow process is needed.

Regarding the resulting solder joint, a fine-grain microstructure and the formation of significantly reduced intermetallic compounds at the copper and solder (63Sn/37Pb) interface have been observed when laser soldering was used as compared to other reflow methods.[12] Stress buildup in the solder joint due to the difference in thermal expansion coefficients between the materials on both sides of the solder joint is expected when the reflow method requires the whole assembly to be exposed to the soldering temperature. Localized heating and exposure of short duration by using a laser are expected to generate less stress in the joint for the assemblies having materials of different thermal expansion coefficients.

5.4.8 Controlled-atmosphere soldering[13]

5.4.8.1 Principle. Based on its function, the atmosphere may be considered as either protective or reactive. A protective atmosphere normally is inert toward a specific soldering material under specific conditions, and a reactive atmosphere may involve either an oxidizing or a reducing function toward the subject system.

Broadly, chemicals that can provide oxidizing or reducing potential in relation to the specific metal-oxide system, and that can generate significant vapor pressure at an operating temperature, are expected to contribute to the functional nature of the total atmosphere.

Following is a list of some commonly used atmospheres. Their corresponding nominal compositions are summarized in Table 5.10.

- Dry air
- Nitrogen
- Hydrogen
- Nitrogen-hydrogen blends at different ratios
- Dissociated ammonia
- Exothermic gas
- Nitrogen dopants at different concentrations

TABLE 5.10 Percentage Composition of Atmosphere Gases

Atmosphere	Carbon dioxide (CO_2)	Oxygen (O_2)	Carbon monoxide (CO)	Hydrogen (H_2)	Methane (CH_4)	Nitrogen (N_2)	Trace
Air	–	21.0	–	–	–	78.1	0.9
Nitrogen	–	–	–	–	–	99.8–100	0–0–0.2
Hydrogen	–	–	–	99.8–100			0–0–0.2
Dissociated methanol	–	–	33.3	66.7	–	–	–
Dissociated ammonia	–	–	–	75.0	–	25.0	–
Exothermic gas (air/gas = 6/1)	5.0	–	10.0	14.0	1.0	70.0	–
Endothermic gas (air/gas = 2.4/1)	–	–	20.0	38.0	0.5	41.5	–

The thermal cracking of methanol essentially yields hydrogen and carbon monoxide at high temperatures, as represented by the chemical equation,

$$CH_3OH = 2H_2 + CO$$

At low temperatures (below 800°C), side reactions may occur, leading to the formation of H_2, CH_4, CO_2, and C.

Each component of the atmosphere gases may function as oxidant or as reducing agent, depending on the temperature and its oxidation-reduction potential relative to that of the materials involved. Among the components of common atmosphere gases, oxygen, water vapor, and carbon dioxide normally serve as oxidants to most metals and metal oxides, and hydrogen and carbon monoxide serve as reducing agents. The ratio of oxidant content to reducing-agent content, in relation to that ratio at equilibrium, indicates whether the resulting atmosphere is oxidizing or reducing.

During soldering, the reactions and interactions of chemicals in the solder paste and between chemicals and the metal surface can be quite complex. In simple terms, the mechanisms may include evaporation, pyrolysis, oxidation, and reduction. The generalized oxidation and reduction reaction can be expressed as follows:

To obtain the thermodynamic equilibrium constant K for each of the preceding reactions,

$$x\mathrm{M}(s) + y\mathrm{O}_2(g) \Rightarrow \mathrm{M}x\mathrm{O}_2(s) \tag{5.1}$$

$$K_1 = \frac{a_{\mathrm{M}_x\mathrm{O}_{2y}}}{a_{\mathrm{M}}^{x}\, a_{\mathrm{O}_2}^{y}}$$

$$\mathrm{M}_x\mathrm{O}_y(s) + y\mathrm{H}_2(g) \Rightarrow x\mathrm{M}(s) + y\mathrm{H}_2\mathrm{O}(g) \tag{5.2}$$

$$K_2 = \frac{a_{\mathrm{M}}^{x} a_{\mathrm{H}_2\mathrm{O}}^{y}}{a_{\mathrm{M}_x\mathrm{O}_y} a_{\mathrm{H}_2}^{y}}$$

$$x\mathrm{M}(s) + y\mathrm{CO}_2(g) \Rightarrow \mathrm{M}_x\mathrm{O}_y(s) + y\mathrm{CO}(g) \qquad (5.3)$$

$$K_3 = \frac{a_{\mathrm{M}_x\mathrm{O}_{2y}} a_{\mathrm{CO}}^{y}}{a_{\mathrm{M}}^{x} a_{\mathrm{CO}_2}^{y}}$$

Assuming that the compositions of solids remain constant and the gases behave ideally,

$$K_1 = \frac{1}{P_{\mathrm{O}_2^y}} \qquad K_2 = \frac{P_{\mathrm{H}_2\mathrm{O}^y}}{P_{\mathrm{H}_2^y}} \qquad K_3 = \frac{P_{\mathrm{CO}^y}}{P_{\mathrm{CO}_2^y}}$$

where a represents the activities of the individual reactants as well as the products of reactions (5.1), (5.2), and (5.3), and $P_{\mathrm{H_2O}}$, $P_{\mathrm{H_2}}$, P_{CO}, and $P_{\mathrm{CO_2}}$ represent the partial pressure of H_2O, H_2, CO, and CO_2, respectively.

By introducing the relationship between the free energy ΔG^o and the equilibrium constant,

$$\Delta G^\circ = -RT \ln K$$

it is shown that reactions (5.1), (5.2), and (5.3) can proceed in the forward or reverse direction, depending on the temperature and the ratios of $P_{\mathrm{H_2O}}$, $P_{\mathrm{H_2}}$, P_{CO}, and $P_{\mathrm{CO_2}}$.

Figure 5.38 shows the standard free energy of formation for some metal-metal oxide systems and CO/CO_2, H_2O/H_2, and CO_2/C atmospheres as a function of temperature. Assuming that they are under equilibrium condition and at a soldering temperature of 250°C, lead oxide and copper oxide can be reduced by hydrogen. However, hydrogen is not effective for tin oxides until the temperature reaches 600°C. Equation (5.2) also indicates that the presence of too much water vapor in the furnace atmosphere will cause oxidation to certain metals. The partial pressure of water vapor should therefore be maintained at a constant and defined value.

At a given atmosphere, composition, and dew point, the gas flow rate and the flow pattern of the exhaust systems in the furnace are also important factors in soldering performance. The gas flow rate should be high enough to avoid localized atmosphere buildup as a result of local reactions. To achieve the best performance and cost results, the required flow rate is determined by the characteristics of the solder paste being used, the furnace belt speed, loading pattern, belt width, and other furnace parameters. The exhaust efficiency

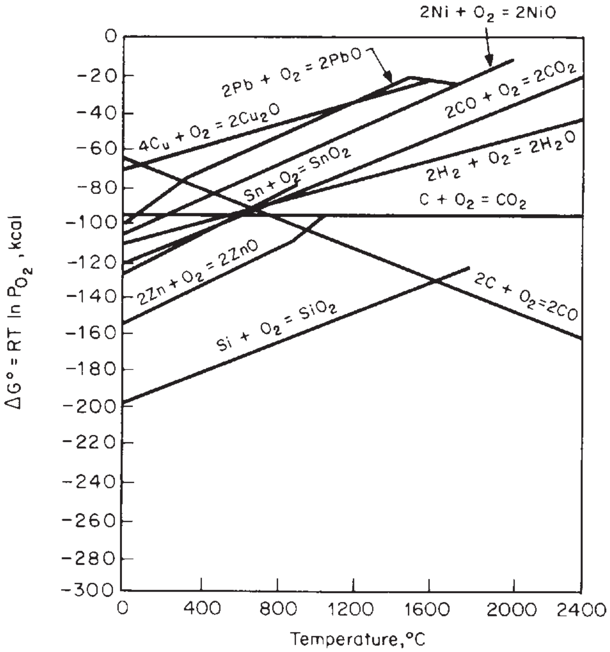


Figure 5.38 Standard free energy of formation for metal-metal oxide systems.

and its flow pattern, in combination with the flow rate, dominate the removal of volatile components generated from the pyroloysis and evaporation of chemicals in solder material, which in turn affects solderability.

It should be noted that a complete burn-out process is normally not feasible at the eutectic tin-lead or tin-lead-silver soldering temperature when using a solder paste. To obtain good solderability and quality solder joints, a metallic continuity at the interfaces between solder and substrate must be formed during soldering. When using a solder paste, a complete coalescence of solder-powder particles has to occur in synchronization with the development of metallic continuity at the interfaces. At the soldering temperature, the atmosphere surrounding the workpiece protects or interacts with the surface of substrates, the solder alloys, and the chemical ingredients in the flux-vehicle system. These interactions determine the chemical and physical phenomena in terms of volatilization, thermal decomposition, and surface-interfacial tension. A controlled atmosphere is expected to deliver a more consistent soldering process.

In addition to consistency, the inert or reactive atmospheres possess further merits. These include

- Solderability enhancement
- Solderability uniformity
- Minimal solder balling

- Irregular residue charring prevention
- Polymer-based board discoloration prevention
- Wider process window
- Overall quality and yield improvement

The inert and reactive atmospheres are expected to facilitate conventional fluxing efficiency during soldering. It should be noted, however, that performance results rely greatly on the specific atmospheric composition and its compatibility with the solder material, substrate, and chemicals incorporated in the system, which must also be compatible with the soldering temperature profile. Figure 5.39 shows that the solderability under N_2 atmosphere is significantly improved, as solder balls that are formed under ambient air conditions are eliminated.

5.4.9 Process parameters[15–18]

5.4.9.1 Gas flow rate. The gas flow rate required to achieve a specific level of oxygen in the dynamic state of the reflow oven is largely controlled by the type

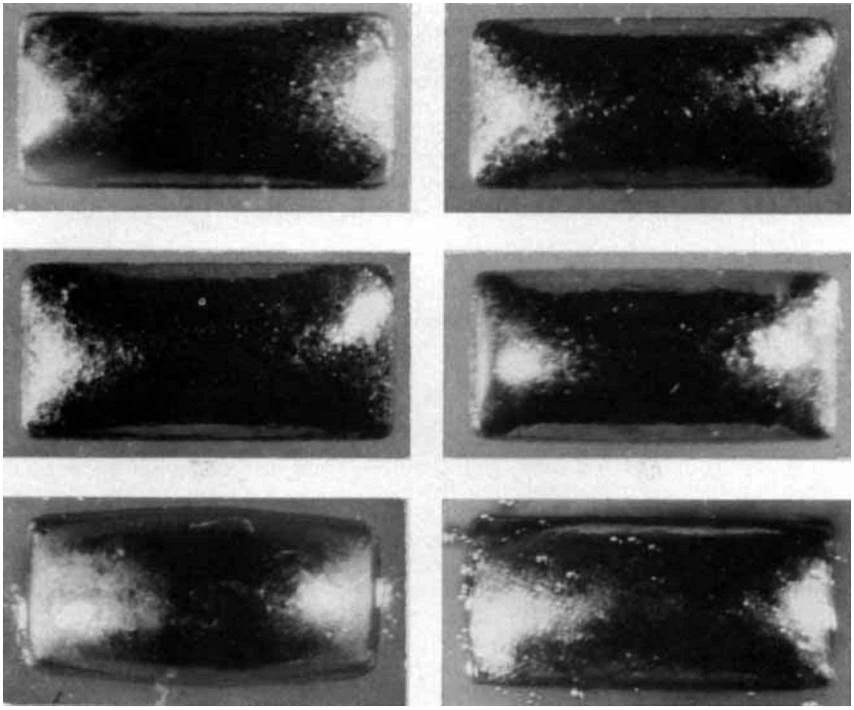


Figure 5.39 Solderability performance of solder paste under N_2 atmosphere vs. ambient air, reflowed under *(a)* N_2, (*b*) $95N_2/5H_2$, (*c*) $85N_2/15H_2$, (*d*) $70N_2/30H_2$, (*e*) H_2, and (*f*) ambient air.

of oven, categorized as closed-system, semi-closed system, or open system. The relationship of the flow rate versus oxygen level within one type of oven and the relationship among the different types of oven are summarized in Fig. 5.40. For a given oven, the required flow rate increases when the allowable oxygen level is lowered. At a given flow rate, when the air tightness in oven construction is reduced, the achievable oxygen level will be higher.

As expected, for a given reflow system, the oxygen level is inversely related to gas flow rate as shown in Fig. 5.41. The gas flow rate also affects the temperature distribution and temperature uniformity of assembly. Figure 5.42 exhibits the temperature gradient between the component PLCC-84 and the board surface, indicating that a higher gas flow rate reduces the temperature gradient of an assembly.[14] However, the downside of using high flow rate goes to the higher gas consumption, therefore increasing cost. The cost impact may be mitigated when the design of oven is capable of internal gas recirculation in an efficient fashion.

5.4.9.2 Humidity and water vapor pressure. Water vapor pressure inside the soldering govern can be contributed from the following:

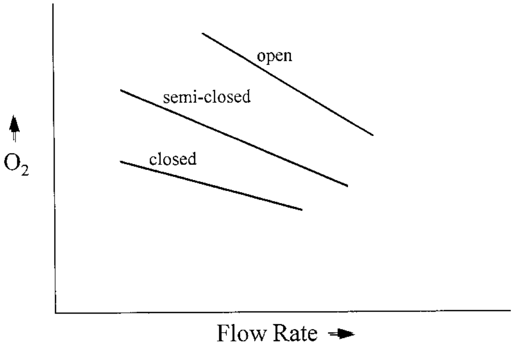


Figure 5.40 Oxygen level of three types of reflow oven.

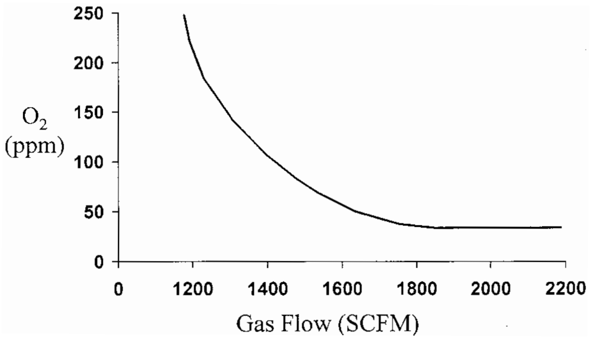


Figure 5.41 N2 flow rate vs. oxygen level.

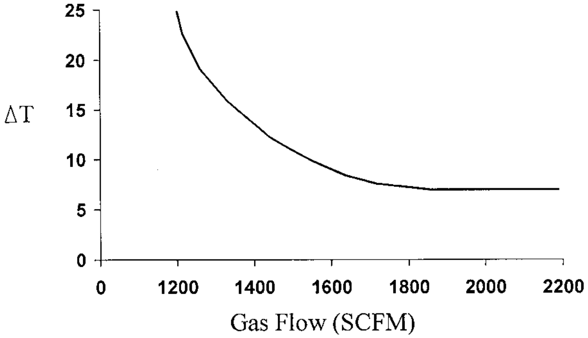


Figure 5.42 Temperature gradient vs. flow rate.

- The composition and purity of atmosphere
- The reaction product of flux/vehicle chemical system with metal substrates
- The moisture release from the assembly including components and board
- The ambient humidity

Because water vapor is essentially oxidizing to metal substrates that are to be joined by soldering, its partial pressure in the oven affects the overall function of the atmosphere.

The partial pressure of water vapor in an atmosphere gas is conveniently expressed as dew point—that is, the temperature at which condensation of water vapor in air takes place. The dew point can be measured by a hygrometer or dewpointer by means of fog chamber, chilled mirror aluminum oxide technique. The relationship of dew point with the vapor pressure is shown in Figs. 5.43 and 5.44. The relative humidity, RH, is related to the actual vapor pressure of water (or represented by dew point), Pw, and the saturated vapor pressure at the prevailing ambient temperature, Ps, as follows:

$$RH = \frac{Pw}{Ps}$$

The purity of incoming gas in terms of moisture is normally monitored by measuring the dew point.

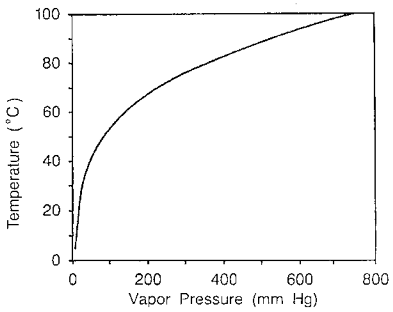


Figure 5.43 Dew point vs. vapor pressure (high).

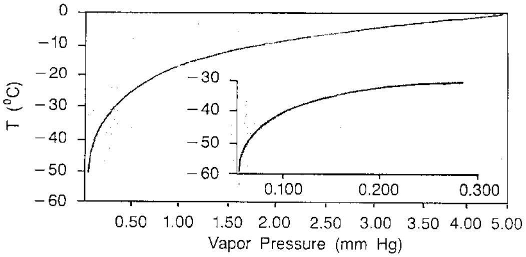


Figure 5.44 Dew point vs. vapor pressure (low).

5.4.9.3 Belt speed. For an evenly spaced loading on the belt, the belt speed not only determines the throughput, it also affects other operating parameters that can alter the soldering results. As examples, the parameters that are affected by the change of belt speed include

- Peak temperature—at fixed temperature settings, increasing the belt speed results in the decrease of peak temperature.
- Atmosphere composition—while other conditions are equal, the change of belt speed may alter the oxygen level (including moisture content).

5.4.9.4 Temperature. The operating temperature or temperature profile is an integral part of soldering process. It affects the physical activity and chemical reaction of the organic system in solder paste or flux. The operating temperature, particularly peak temperature, changes the wetting ability of molten solder on the metal substrate; wetting ability generally increases with increasing temperature. Chemical reactions and thermal decompositions respond to the rising temperature and the temperature profile.

5.4.9.5 Oxygen level. Various studies have focused on the application of no-clean processes and on the determination of the maximum allowable oxygen level for using nitrogen-based no-clean soldering process in solder paste reflow and wave soldering.

Each study was performed with a specific solder paste and flux or with a selected series of paste and flux. Tests were conducted with specific equipment under a designated process. In view of the continued introduction of new equipment and the diversity of processes coupled with the versatility of solder paste and flux compositions, the test results are expected to represent the specific system (paste, oven, process, assembly) and at best to provide a guideline reference point. For example, a solder paste from the Vendor I to be used with Process A may require a maximum 20-ppm oxygen level to obtain good solderability, freedom from gross solder-ball effects, and acceptable after-soldering residue. To achieve similar results, the same paste to be used with Process B may need a maximum of 300 ppm oxygen. The same could be true for a different paste used in the same process.

The precise oxygen level requirement for a no-clean soldering is impractical to pin down. Instead, the general principle and trends in the relationship between the performance feature and the allowable maximum oxygen level can be derived. Figure 5.45 presents the trend of performance feature merit in relation to oxygen level for a series of solder paste containing various levels of solid contents. For a given performance feature, Fig. 5.46 shows the trend of the effect of solid content in no-clean paste on oxygen level requirement during reflow soldering. The performance feature denotes the solderability or the reduction in solder balling.

For convenience, solderability may be monitored by measuring wetting time, wetting force, meniscus rise, or wetting angle, or by visual wetting quality. The series of the curves represents the generic groupings of no-clean solder paste or flux by the level of solid contents. This is, however, based on the fact that the solid content possesses a good flux system. As shown in Fig. 5.45,

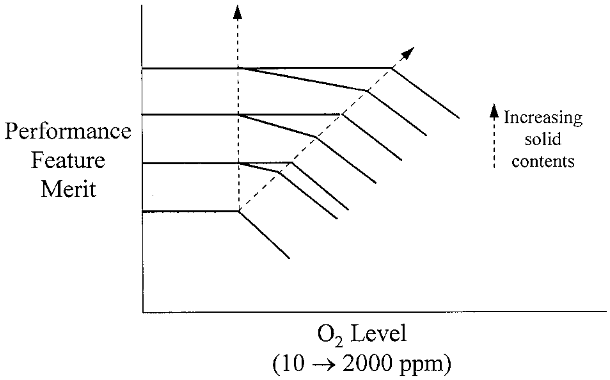


Figure 5.45 Dew point vs. vapor pressure (high).

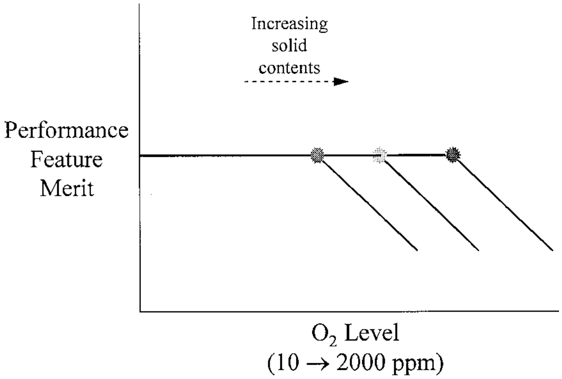


Figure 5.46 Solid content in paste vs. performance feature.

the performance trend in the increasing solderability and decreasing solder balling is enhanced when the solid content increases, and, at a given solid content beyond a threshold of oxygen level, the performance will significantly drop. It should be noted that increasing solid content creates an increasing amount of after-soldering residue. The required oxygen level may fall in any place within the region, depending on other factors as discussed above. For a given level of performance, the allowable oxygen level will be relieved as the solid content increases, as depicted in Fig. 5.46.

5.4.9.6 Optimal O_2 level. In general, with levels higher than 2,000 ppm O_2, the effect of nitrogen may hardly be detected. Below 20 ppm O_2, the process will become difficult to control and, needless to say, too costly. For a given oven and process, the required O_2 level is essentially controlled by the chemistry and makeup of the solder paste. For example, a solder paste from Supplier A may require a maximum level of 800 ppm O_2 to obtain the desirable results (good wetting, no solder balls, etc.). To achieve similar results, solder paste from Supplier B may need a maximum of 200 ppm O_2. In practice, O_2 levels in the range of 20 to 2,000 ppm should be able to accommodate most applications.

Soldering under nitrogen poses two additional demands: more stringent process control and higher operating cost. However, its potential effects on solderability, heat transfer, PCB materials, and process window may bring benefits in mounting large-area and heavy BGAs as well as in connecting small and delicate CSPs onto complex PCBs.

5.4.10 Profile temperature measurement

At a steady state, and when properly used, the thermocouple can readily measure true temperature. However, in a dynamic environment, such as the reflow process, the response efficiency of a thermocouple may affect the accuracy of the temperature measurement.

To accurately measure the temperature on a solid surface (or a point), the thermocouple must be in a direct and firm contact with the surface to be measured. It is common to use attaching materials such as a high-temperature solder and high-temperature adhesive or Kapton® tape. The application of any of these materials inevitably introduces an additional mass into the contact area, which works as a thermal sink. The additional mass may skew temperature readings, resulting in an understanding readout. For cases in which the tip of the thermocouple is broken away from the surface contact, the oven air temperature, rather than the intended surface temperature, may be recorded. Thus, the amount of solder or adhesive used should be as small as possible, minimizing the barrier in heat transfer and thermal mass.

A more desirable technique, however, is to make contact without the use of extraneous material. One system (by Saunders Technology) has demonstrated its usefulness and performance. Its design features include a unique thermocouple probe mounted in a sliding ball joint and a detachable clamp. The probe serves as the temperature sensor, composed of a thermocouple hermetically sealed in a nominally 0.020-in (0.51-mm) diameter stainless steel sheath. The sliding ball joint provides the positioning flexibility to reach a specific location on the board. Each clamp secures one or two probe sensors to the edge of the board, and multiple clamps can be used for simultaneously monitoring the temperature at selected locations. The probe can be readily connected to most commercially available profilers for data processing. A firm contact that can accommodate any possible shift during the temperature excursion is obviously a crucial element. A small-diameter probe tip also offers flexibility in access.

A low-mass, direct, firm contact, without the need for extraneous attachment material, provides a way to meet the criteria for achieving accurate temperature measurement.

5.5 Solderability[1]

5.5.1 Definition

Solderability, in a broad sense, is the ability of achieve a clean metallic surface on substrates to be joined during a dynamic heating process so that a good wetting of molten solder on the surface of the substrates can be formed. When using solder paste, solderability requires the additional ability to achieve a clean metallic surface on the solder powder so that a complete coalescence of the solder powder particles can be obtained. Solderability relies on the fluxing efficiency provided by fluxes or the solder paste and on the quality of the surface of the substrate.

5.5.2 Substrates

Among the common substrates to be soldered, the demand placed on the flux for good wetting depends on the intrinsic wettability of substrates. The wettability is ranked in the order of Sn, Sn/Pb > Cu > Ag/Pd, Ag/Pt > Ni. Solderability may change as a result of variations in the quality of the substrate surface. Therefore, using the same flux system may not produce the same results if the substrate surface condition varies.

The demand on flux strength also depends on the reflow temperature and techniques. Convection reflow operation under ambient atmosphere requires more fluxes than vapor-phase, hot air, or laser reflow. Inert or reducing atmospheres can modify the reflow performance in terms of wetting as well as residue characteristics.

5.5.3 Wetting phenomena

Good wetting is visualized as the formation of a smooth, uniform, and continuous solder coating on the surface of solder pads without dewetting, nonwetting, or pinholes.

Dewetting is the phenomenon of molten solder receding after it has coated the surface, leaving a rough and irregular surface with thick mounds of solder connected by thin solder film. In dewetting, the substrate surface is not exposed. *Nonwetting* is defined as the phenomenon of molten solder not adhering to the substrate surface, thereby leaving the substrate surface exposed. The molten solder in such a case tends to form a high wetting angle (>90°).

5.5.4 Solderability of components

Component leads are commonly made of copper, copper alloys, Alloy-42 (41 to 42.5 percent nickel, the balance iron), and Kovar (2 percent nickel, 17 percent cobalt, 53 percent iron, 1 percent others).

The leads are normally coated with a coating composition in a range of tin-lead alloys by means of aqueous plating or molten solder dipping. The plating process provides more uniform thickness, which is often porous, and molten solder dip produces a thicker and denser fused coating.

Ideally, device leads are pretinned to assure good solderability. But in practice, after tinning, most components undergo operations such as lead forming, encapsulation, or burn-in. These steps can degrade the surface quality of the lead significantly and, therefore, affect solderability. In summary, the solderability of tinned leads depends on the following factors:

- Composition of base lead materials
- Composition of coating
- Surface finish and condition of coating
- Age of coating
- Storage of coating
- Thickness of coating

A coating thickness of 0.0003 in (7.6 µm) is most prevalent, and a thin coating is often associated with poor solderability. Nonetheless, the ideal coating thickness depends on several practical factors.

The solderability of coated leads, under various shelf times and conditions, is a concern. Assuming that the coating is intact, this concern can be viewed from two aspects: (1) how is the solderability affected by the surface degradation due to oxidation or contamination during shelf time, and (2) how is the solderability affected by the interaction between lead material and tin-lead coating during shelf time or a treatment such as a burn-in test. The surface oxidation of tin-lead alloys normally is not an unsolvable problem, because the fluxing is able to take care of it.

The formation of copper-tin intermetallic compounds at the interface of copper-based leads and tin-based coating (Cu_3Sn, Cu_6Sn_5) can readily occur, although it would be extremely sluggish at room temperature, as indicated in the Cu-Sn phase diagram. With this interaction, the tin content at the coating–lead interface will be consumed gradually, resulting in solderability degradation. The consumption rate depends on temperature and time. In this regard, Alloy-42 and Kovar leads are expected to do better than copper leads with high-tin coating. However, high-tin coating normally provides better wettability.

It should be noted that, for leads coated by molten solder dip, copper-tin intermetallic compounds (namely, Cu_6Sn_5) can be formed rapidly during coating. However, because of its intactness, the molten solder dip coating is expected to be relatively more stable during storage than electroplating. Leads made of Alloy-42 and Kovar may experience deterioration with age as a result of moisture permeation through the porous crystalline structure.

In either case, the degradation of the coating is driven by a kinetically controlled process and depends on other practical and environmental factors. Therefore, to assure the quality of the coated surface of leads, the shelf time and storage temperature must be minimized. Using freshly coated leads is ideal.

Component leads can also be coated with palladium. The compatibility of solder paste and reflow profile determines the solderability.[2]

5.5.5 Surface finish of PCBs

Section 5.8.5 provides a description of PCB surface finish characteristics.

5.6 Cleaning

5.6.1 Principle and options

After soldering, the residue surrounding the solder joint can be either removed (cleaned) or left as is. The decision about whether to clean up the residue depends on the property and activity of the residue and the reliability desired under specified service conditions.

Residual water-soluble chemistry left on or around solder joints after soldering need to be cleaned. The residue from liquid flux can be a simple system composed of a small amount of organic acid, high boiling solvents, surfactant, and reaction products. Residues from paste may contain a mixture of ingredients, including polar organics, nonpolar organics, ionic salts, and metal salts.

Key steps in a typical cleaning process are prerinse → wash → rinse → final rinse → drying. The parameters that affect the cleaning efficiency include

- Temperature of water
- Spray pressure
- Spray angle
- Wash time
- Flow rate
- Agitation aid

When a compromise among the parameters is needed, higher temperature and higher spray pressure often play more important roles than the flow rate and spray angle. In addition, mechanical agitation aids in dislodging foreign matter from the board and the clearance between components and the board. Ultrasonic agitation and centrifugal energy can provide effective mechanical force. Centrifugal force that is directly proportional to the square of angular velocity and its parallel direction to the board assist the cleaning operation. Ultrasonic cleaning employs cavitation, defined as the implosion of microscopic vapor cavities within the solution, which is induced by the changing pressure differentials in the ultrasonic field. The pressure differentials are created by the exchange between negative and positive pressure in a liquid region. When the liquid with negative pressure is created, its boiling point drops, and many small vapor bubbles are formed. As the pressure changes to positive, the small bubbles implode with great violence. The mechanical wave is generated by high-frequency electrical energy released by a transducer. The cavitation phenomenon provides mechanical agitation and a scrubbing effect.

The effectiveness of ultrasonic cleaning depends on the cavitation intensity, which in turn is controlled by the magnitude of power or pulse width and by dissolved air in the solution. The effect of dissolved air has been illustrated and tested, indicating that it can act as an acoustical screen and energy absorber.[19] A deaeration step is needed to remove the air so as to obtain the true vaporous cavitation. It is suggested that the high audible noise level (a pronounced hissing sound) and minimal visible bubbles in solution, coupled with violent surface activity, are signs of ultrasonic efficiency. It is also suggested that the temperature of the solution is a factor in ultrasonic efficiency. The desirable temperature is approximately in the range of 80 to 98 percent of the boiling point of the solution.

Because of the concern that ultrasonics may damage wire bonding or other chip components, compatible process parameters are to be identified. Some guidelines are proposed as follows:

▪ Power of ultrasonic cleaner:	30 W per liter
▪ Ultrasonic range:	30 to 66 kHz
▪ Cleaning time:	3 min/cycle for five cycles (not to exceed a total of 15 min)

Because of the narrow gap (clearance) between the components and the board in surface mount assemblies, ensuring cleanliness has always been a problem. To solve the dilemma of cleaning process efficiency and the accuracy of cleanliness measurements, a functional test—the surface insulation resistance test—provides an indication of the cleanliness level for a given assembly. Cleaning efficiency on the production line, however, should rely on the established process and its stringent control, and the tests merely provide confirmation.

5.7 Fine-Pitch Application

In addition to the selection of solder paste, major factors contributing to the the results in printing solder paste include stencil thickness versus aperture design, stencil aperture versus land pattern, and stencil selection.

5.7.1 Stencil thickness vs. aperture design

When printing solder paste, proper design of the relative dimensions of stencil thickness and stencil aperture is required to achieve a balance between the printing resolution and the proper amount of solder deposit, thereby avoiding starved solder joints and pad bridging. For a selected stencil thickness, too small a stencil aperture width leads to open joints or starved joints. Too large an aperture width causes pad bridging. Table 5.11 provides guidelines for designing stencil thickness in relation to aperture.

TABLE 5.11 Guideline of Stencil Thickness vs. Aperture Width

Component lead pitch		Aperture width		Maximum stencil thickness	
inch	mm	inch	mm	inch	mm
0.050	1.26	0.023	0.58	0.0140	0.35
0.025	0.63	0.012	0.30	0.0075	0.19
0.020	0.50	0.010	0.25	0.0063	0.16
0.015	0.38	0.007	0.18	0.0043	0.11
0.008	0.20	0.004	0.10	0.0025	0.06

5.7.2 Stencil aperture design vs. land pattern

To make solder joints using a one-pass printing process, the stencil thickness must be selected such that it transfers a sufficient amount of paste onto the non-fine-pitch solder pads while avoiding an excessive paste deposits on the fine-pitch pads. Several options are available to achieve the deposition of a proper amount of solder paste on the land pattern to accommodate a mix of sizes of solder pads. These are enumerated below.

1. *Step-down stencil.* This is commonly achieved by chemically etching the non-fine-pitch pattern area from one side of the stencil while etching the step-down area for the fine-pitch pattern on the other side during a double-sided etch process. Alternatively, step-down area is etched into one foil, and a non-fine pitch pattern is etched into the other foil, after which the two foils are registered and glued together.

   The practical step gradient is 0.002 in (0.05 mm), and some common combinations are

   0.008 in (0.20 mm) for non-fine pitch

   0.006 in (0.10 mm) for fine pitch

   or

   0.006 in (0.15 mm) for non-fine pitch

   0.004 in (0.15 mm) for fine pitch

2. *Uniform reduction on four sides of apertures.* The dimensions of the fine-pitch aperture on stencil are reduced by 10 to 30 percent in relation to those of the land pattern. This reduces the amount of paste deposition on fine pitch land pattern and also provides some room for printing misregistration and paste slump, if any.

3. *Staggered print.* The opening in the stencil is only one-half the length of the solder pad and arranged in an alternating manner as shown in Fig. 5.47. For tin-lead coated solder pads, when the paste starts to melt during reflow, the molten solder is expected to flow to the other half of the pad, making the coverage complete. With a bare copper or nickel surface, the molten solder may not flow out to cover areas where the paste has not been printed.

4. *Length or width reduction.* The dimensions of the stencil opening are reduced along the length or width by 10–30 percent in relation to that of solder pads, achieving the reduction of the amount of paste deposited.

5. *Other shapes.* The stencil openings are made with selected shapes, such as a triangle or teardrop, to achieve the reduced solder paste deposition on fine pitch pattern.

6. *Compromise stencil thickness.* Instead of using the specific thickness that is considered to be the most suitable for a specific land pattern, select a thickness that is practical to both fine-pitch and non-fine-pitch patterns. For example,

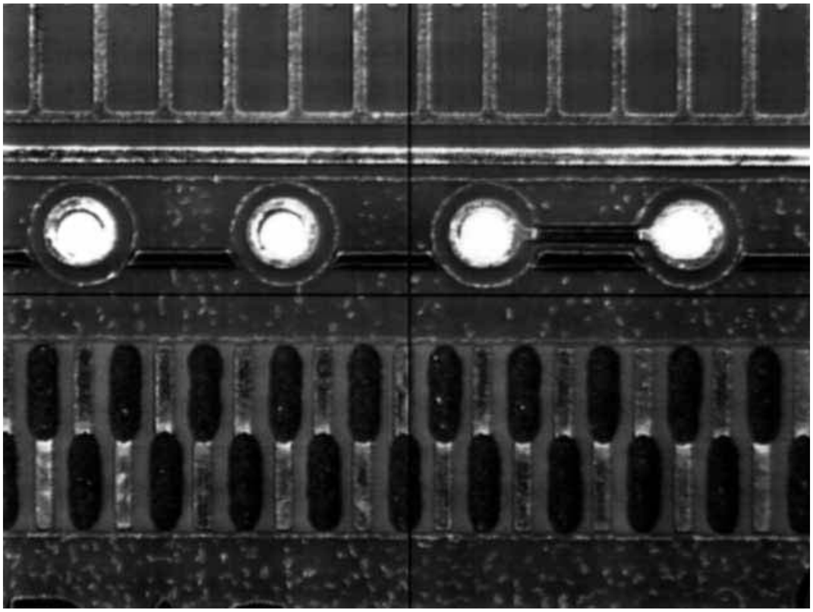


Figure 5.47 Staggered print.

Land pattern pitch combinations		Compromise stencil thickness	
mil	mm	inch	mm
50 and 25	1.26 and 0.63	0.007–0.008	0.18–0.20
50 and 20	1.26 and 0.50	0.006–0.007	0.15–0.18

5.7.3 Stencil selection

The performance of stencils is primarily driven by the foil metal and the process used to create the printing pattern. Currently, five types of stencil materials are commercially available—brass, stainless steel, molybdenum, Alloy-42, and electroformed nickel. The processes making the stencils may involve chemical etching, laser cutting, electropolishing, electroplating, and electroforming. Each type of foil or fabricating process possesses inherent merits and limitations. The key performance of a stencil is assessed in terms the straightness of the vertical wall, wall smoothness, and dimensional precision. In addition, durability, chemical resistance, fine opening capability, and cost are also important factors.

Table 5.12 compares various stencil materials, and Table 5.13 summarizes the relative performance characteristics of stencil-making techniques.[2]

TABLE 5.12 Comparison of Stencil Materials in Key Performance Areas

Performance	Brass	Stainless steel	Molybdenum	Alloy–42	Ni (electroforming)
Mechanical strength	unfavorable	favorable	favorable	favorable	favorable
Chemical resistance	unfavorable	favorable	unfavorable	favorable	favorable
Etchability	favorable	favorable	favorable	favorable	N/A
Sheet stock availability	favorable	favorable	unfavorable	favorable	N/A
Cost	favorable	less favorable	unfavorable	less favorable	N/A
Fine pitch (openings) capability	favorable	may need electropolishing	favorable	may need electropolishing	favorable
Unique feature	lowest cost	durable	self-lubricating, smooth wall	–	finest opening

5.8 Soldering-Related Issues[2]

5.8.1 Intermetallics vs. solder joint formation

Intermetallic compounds have often been observed at or near the solder/substrate interface as well as in the interior of solder joints. Metallurgically, an intermetallic compound is one type of intermediate phase that is a solid solu-

TABLE 5.13 Comparison of Techniques in Building Stencils

Techniques	Characteristics	Capabilities or features
Chemical etching	Most established process, sensitivity of fine pitch capability to process and control, sensitivity of aperture size and vertical wall control	Versatile, economical
Laser cut	Grainy wall surface; sequential cut, not concurrent formation of openings; higher cost; difficulty in making step stencil	Fine pitch capability, no photo tools or resist needed
Electropolishing	Complementary step to produce smooth wall surface	Smooth wall surface
Ni-plating on aperture wall	Reducing aperture opening, smooth surface	Finer opening
Electroforming	Additive process via electrode position, concern about foil strength, difficulty in making step stencil, suitable for stencil thickness of 0.001 in to 0.012	Gasket effect minimizing bleedout, capability of producing very fine opening, no need for electropolishing

tion with intermediate ranges of composition. Intermetallic compounds form when two metal elements have a limited mutual solubility. These compounds possess a new composition of a certain stoichiometric ratio of the two elements.

The new compositions have a different crystal structure from those of their elemental components. The properties of the resulting intermetallic compounds also differ from component metals in that they exhibit reduced ductility, density, and conductivity. Tin or tin/lead solder is metallurgically active with most metals that are commonly used in electronics packaging and assembly. Various intermetallic compositions have been identified under the equilibrium condition between tin and substrate metals, such as Au, Ag, Cu, Pd, Ni, and Pt. Indium-based solders also interact with these substrate metals, often forming intermetallics. One should note that thermodynamically stable compounds may not always be present, and some intermetallics that do not appear in the equilibrium phase diagram have been identified in soldered systems.

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 95Sn/5Sb and 96Sn/4Ag solder.
- Intermetallics are developed during a service life either along the interface and/or in the interior of the solder joint.

When solder comes in contact with a common metal substrate for a sufficient amount of time at a high enough temperature, intermetallic compounds may form. Below a solder's liquidus temperature, formation is primarily a solid state diffusion process and thus depends to a great extent on temperature and time. While solder is in a molten state, the solubility of the element from substrate into molten solder accelerates the rate of intermetallic formation.

External factors such as the temperature of exposure and the time at the elevated temperature also affect the rate of intermetallic compound formation. Thus, solder reflow conditions such as peak temperature, and the total dwell time at elevated temperatures, influence the rate and extent of intermetallic growth. Also, while in storage or service, the exposure of the assembly is a factor for intermetallic growth in systems.

The thickness of growth between eutectic tin/lead and copper is proportional to the square root of time, coinciding with the diffusion-controlled kinetics. As temperature rises, the rate of formation increases, with the longer time promoting the process.

The composition of intermetallics at the interface may differ from those of the solder joint interior. Furthermore, the surface condition of the substrate affects the kinetics of intermetallic development. For example, the oxidized surface may show a delayed development of the intermetallic phases, making a thinner layer as compared with a clean surface for a given amount of time. Unlike high-tin-content solder, which tends to form intermetallic compounds with small crystal structures, high-lead-content solder forms high, needle-like crystals.

In brief, the extent of intermetallic formation, the composition of the compounds, and their morphology depend on intrinsic factors. These factors include the following:

- The metallurgical reactivity of a solder with a substrate
- Soldering (reflow) peak temperature
- Dwell time at peak temperature
- The surface condition of a substrate—clean versus oxidized
- The post-soldering storage and service conditions

Intermetallics at the interface can be beneficial or detrimental. Wetting on the substrate followed by the formation of a thin layer of intermetallics is the prevalent mechanism in making permanent solder bonds. However, adverse effects may occur if the intermetallic layer becomes too thick. Generally acceptable thickness falls in the range of 1 to 5 μm.

The morphology, size, and distribution of intermetallics in solder determine their beneficial or detrimental effects on solder-joint integrity. If they possess the correct properties, the intermetallics in the interior of the solder joint (away from the interface) act as a strengthening phase. In contrast, large and needle-shaped compounds generally weaken the mechanical properties of a solder joint.

The formation of excessive intermetallic compounds has proven to be a frequent source of solder joint failure. Cracks are often initiated around the interfacial area under stressful conditions when an unacceptable amount of intermetallic materials develop along the solder/substrate interface.

The adverse effect of intermetallic compounds on solder-joint integrity is believed to be attributed to the brittle nature and thermal expansion properties of such compounds, which may differ from the interior solder. The difference in thermal expansion contributes to a solder's internal stress development. In addition, excessive amounts of intermetallic compounds impair the solderability of some systems, depleting one element of the contact surface. For instance, tin depletion from tin/lead coating on copper leads causes the exposure of Cu_3Sn to oxidation, resulting in inconsistent and/or poor solderability of component leads. In this case, the interface area is composed of gradients with Cu_3Sn phase next to the copper substrate followed by Cu_6Sn_5 phase and lead-rich phase away from the interface line. Also, excessive intermetallics render a dull, rough look to solder joints.

A precise bonding process for die attach involving in-situ formation of Cu-Sn intermetallics from vapor-deposited copper-tin multilayer has been introduced. The unique feature of this bonding process is its fluxless nature and its control of intermetallic thickness. The resulting joint is composed of uniformly distributed Sn and Cu_6Sn_5 with a joint thickness of 4.5 µm.

The role of intermetallics, beneficial or detrimental, is determined by the design of an assembly, the service conditions in relation to that design, and the control of the soldering process. Understanding the relationship among them is the key to making reliable solder joints.

5.8.2 Gold-plated substrates vs. solder joint formation[2]

Using gold (Au) as a surface coating to resist the oxidation of underlying metals in semiconductor packages and electronics assemblies is a routine practice. Common applications include gold plating on PCBs, gold-containing thick film circuitry on hybrids, soft gold (24 karat) wire bonding, and hard gold (cobalt or nickel gold) for edge fingers as connectors. However, many in the industry are concerned or uncertain about the full role gold plays in solder.

When a gold-coated substrate is in direct contact with an Sn/Pb solder, the Au combines with the Sn of the solder at a rapid rate as a result of the metallurgical affinity between Sn and Au, forming Au-Sn intermetallics. Gold-tin intermetallics can affect a solder's physical and mechanical properties and alter a solder joint's appearance and microstructure.

An Au concentration below 10 percent by weight in Sn/Pb solder slightly increases that solder's initial tensile strength. However, beyond 3 percent, a solder's shear strength slowly drops. Normally, its hardness increases with the addition of gold. This effect is enhanced as the Au content exceeds 7 percent. A solder's ductility is slowly reduced with Au concentrations below 7 percent by weight and then drops rapidly as the Au content exceeds 7 percent by weight.

Gold can affect a solder's ability to wet and spread. Although a 2 percent Au concentration has no effect on 63Sn/37Pb, concentrations above 2 percent reduce the solder's spreadability and fluidity. For copper plated with Au, a pure Au coating has shown better wetting and spread than alloy Au when soldering with 63Sn/37Pb under identical conditions.

The dissolution rate of Au in solder depends on temperature, time, and solder composition. Foreign elements (e.g., Au, In, and Zn) in Sn/Pb solder retard this dissolution. During a reflow process with a long heating time, the quick dissolution of Au in molten solder causes that solder to wet directly onto the base metal and not the gold coating.

Although one might expect gold's inert nature to provide a base metal with full protection, tests on the aging of gold-electroplated Cu indicate that the solderability as measured by wetting time degrades with aging at a temperature of 170°C. Solderability degrades from the following causes:

- Diffusion of atmospheric contaminants through the porous Au film results in the oxidation the base material.
- Diffusion of base metal reaches the surface through the coating. The diffusion rate is associated with the Au coating grain size, with smaller grain sizes favoring diffusion.

Gold dissolved in solder alters that solder's microstructure. As the Au content reaches 1 percent by weight, the characteristic needle-shaped phase found in eutectic solder becomes readily detectable in the microstructure. The amount of hard phase increases with elevated Au concentrations. At room temperature, the composition of these intermetallics is a mixture of $AuSn_4$ and Sn.

The incorporation of Au may or may not change a solder's physical properties. At concentrations below 10 percent by weight, Au does not significantly affect a solder's electrical or thermal conductivity.

Gold can lower a solder's solidus temperature and increase its liquidus temperature, thereby widening the paste range or creating a pasty range for eutectic solder. This affects a solder's application performance, particularly for solder interconnections. Lowering a solder's softening temperature changes its mechanical response to rising temperatures. A eutectic solder is required for applications demanding high solder fluidity, whereas assemblies with a wide gap to fill find solder with a wide pasty range preferable.

Overall, Au has the most pronounced effect on solder joints in the following areas:

- Fluidity
- Wettability and spread
- Mechanical properties
- Phase transition temperature
- Microstructure
- Appearance

An overly thick Au coating results in a higher Au concentration in solder and an increase in material cost. If the coating is too thin, the surface protection effectiveness may suffer. One should also take into account that the surface condition of Au, particularly its porosity, is equally important to surface protection. An optimal Au application balances surface intactness, concentration in solder after dissolution, and cost.

When a solder's Au content is excessive, the following mechanical and/or metallurgical phenomena may occur:

- Premature solder joint fracture due to embrittlement
- Void creation
- Microstructure coarsening

The upper limit of Au concentration is assessed to be 3 percent by weight. Above 3 percent, deleterious effects could occur in one or more of the aforementioned areas. The 3-percent limit cited here is only a guideline. As a rule, one should verify the effect of Au concentration in solder for its performance in a specific electronics package and assembly under a given set of conditions.

To ensure that Au concentrations do not exceed acceptable levels, industry standards call for Au removal immediately prior to soldering. The general guidelines for Au removal are as follows:

- A double tinning process of dynamic solder wave must be used for proper Au removal.
- An Au removal procedure is unnecessary for through-hole components intended for dip or wave soldering, provided that the Au on the leads is less than 0.0025 mm.
- For surface mount parts, Au must be removed from at least 95 percent of the surface to be soldered.

5.8.3 Solder-joint voids

Voiding is one of the adverse phenomena in solder-joint integrity and reliability. It is generally expected that a low volume of small, well dispersed voids has little effect on solder-joint integrity; however, high-volume or large-size voids can degrade the joint with respect to its electrical, thermal, or mechanical properties.

For solder joints made from solder paste, the flow characteristics and the thermal and physical properties of the vehicle-flux system, as well as the metal load, are important factors. To minimize voiding, the processing parameters and joint design should be optimized. These include the dosage of paste deposit, deposit thickness, joint configuration, reflow time, cooling rate, and wettability. The same paste could generate different voiding in size and concentration if used under varying conditions. A quality joint is, therefore, influenced equally by the solder-joint assembly process and the quality of the paste. Further discussion can be found in Ref. 2.

5.8.4 Solder balling/beading

When using solder paste, solder balling in the reflow process is a common phenomenon. A continuous effort has been made through soldering process control, component and board quality assurance, and solder paste design to minimize the occurrence of solder balling.

The solder balling phenomenon can be defined as the situation that occurs when small spherical particles of various diameters are formed away from the main solder pool during reflow and do not coalesce with the solder pool after solidification, as shown in Fig. 5.48. Various manufacturing environments have revealed two distinct types of solder balling in terms of physical characteristics:

A. Solder balling around any components and over the board

B. Large solder balls associated with small and low-clearance passive components (e.g., 0805, 1206), with most of them being larger than 0.005 in (0.13 mm)

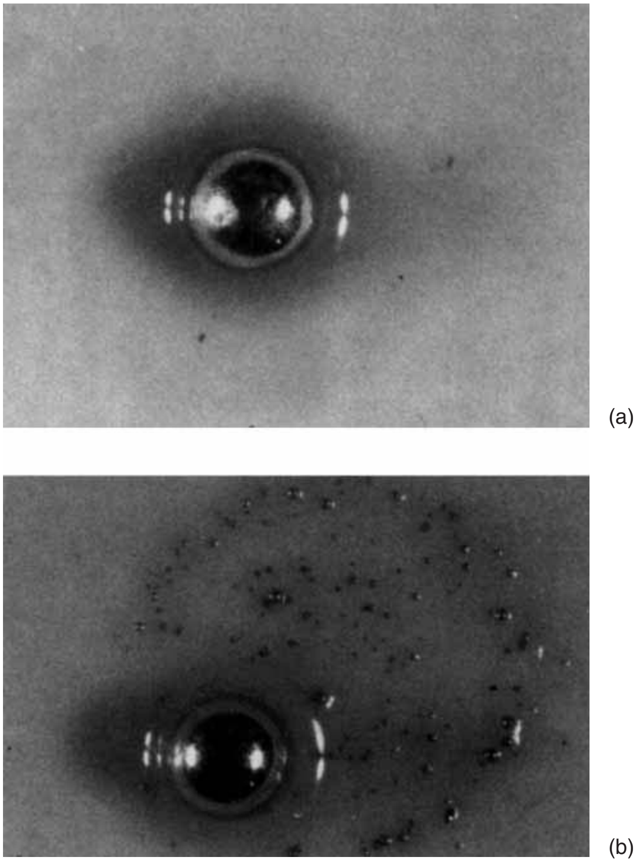


Figure 5.48 Solder balling.

The type (A) solder balls normally can be removed during cleaning; type (B) solder beads, however, are difficult to remove using a normal cleaning process. With the implementation of a no-clean process, it is obviously desirable to avoid the occurrence of both types of solder balling. With the use of array packages (BGAs), solder balling also becomes more troublesome. In the presence of solder balls, the assembly may encounter the risk of electrical short when any solder balls become loose and mobile during service. Excessive solder balling may also deprive solder from making good solder joint fillet. In general, type A solder balls can be formed for different reasons. The following are the likely sources that should be considered:

- Solder paste with inefficient fluxing with respect to solder powder or substrate or reflow profile can result in discrete particles that do not coalesce, caused by either the paste design or subsequent paste degradation.
- Incompatible heating with respect to paste prior to solder melt (preheating or predry) can degrade the flux activity.
- Paste spattering caused by excessively rapid heating can result in the formation of discrete solder particles or aggregates outside the main solder pool.
- Solder paste that is contaminated with moisture or other high "energy" chemicals that promote spattering can produce solder balls.
- Solder paste that contains extra-fine solder particles that are carried away from the main solder by the organic portion (flux/vehicle) during heating can result in small solder balls.
- Interaction between solder paste and solder mask can cause the problem.

The appearance and distribution of solder balls often reveal the cause. Solder balls as a result of spattering are usually irregular and relatively large in size (larger than 20 µm is not uncommon) and are scattered over a large area of the board; solder balls caused by fine powder in the paste often form a halo around the solder; ineffective or insufficient fluxing results in small solder balls that are scattered around the joint; and solder mask-related solder balls leave discoloration marks on the board.

Solder paste spattering during reflow can caused by the following phenomena:

- Incompatibility between paste and reflow profile, such as excessively fast heating; high volatile content in the paste.
- The hygroscopicity of the paste; when the open time during assembly exceeds the capability of the paste or the paste is exposed to temperature and/or humidity beyond its tolerance level, the moisture absorbed by the paste can cause spattering.

To minimize solder balling during board assembly, several issues need to be addressed.

- Selection of a solder paste that is able to deliver performance under the specific production conditions
- Understanding the characteristics of the solder paste selected
- Setup of the reflow process that best fits the solder paste selected
- Assurance of consistency and quality of the solder substrate, including boards and components
- Control of ambient conditions (temperature and humidity)
- Control of open time that the paste can accommodate
- Assurance of solder mask compatibility with the solder paste
- Assurance of a complete cure of the solder mask

For large solder beads associated with small passive components, formation is largely attributed to the paste slump and flow under the component body, between the two terminations, via capillary effect. The slump and flow dynamics can also be affected by the reflow temperature profile, the volume of paste, and component placement. To reduce the occurrence of these large solder beads, the following parameters are recommended for consideration:

- Solder paste rheology—minimizing paste slump
- Amount of solder paste deposit—avoiding excess paste
- Component placement—avoiding paste spread during placement
- Reflow profile—reducing preheating temperature exposure

5.8.5 PCB surface finish

For making sound interconnections, the characteristics and properties of the circuit board surface finish are as important as the component leads and termination.

Hot air solder leveled SnPb (HASL) has been used successfully as the surface finish for surface mount and mixed PCBs. As the need of a flat surface with uniform thickness becomes increasingly important to forming consistent and reliable fine-pitch solder joints, the HASL process often falls short. Alternatives to HASL include immersion Sn, electroplated SnPb (reflowed or nonreflowed), electroplated Au/Ni, electroless Au/electroless Ni, immersion Au/electroless Ni, immersion Pd, immersion Pb/electroless Ni, electroplated Sn-Ni alloy, and organic coating. When selecting an alternative surface finish for a PCB assembly, the key parameters to consider are solderability, ambient stability, high-temperature stability, suitability of the use as contact/switch surface, solder-joint integrity, wire bondability of assemblies that involve wire bonding, and cost.

5.8.5.1 Basic process. The three primary techniques to deposit metallic surface finish are electroplating, electroless plating, and immersion. Inherently, electroplating utilizing electric current is capable of economically depositing thick coatings up to 0.000400 in, depending on metal and process parameters. Electroless plating, requiring the presence of a proper reducing agent in the plating bath, converts metal salts into metal and deposits them on the substrate. The immersion plating process, in the absence of electric current and reducing agent in the bath, deposits a new metal surface by replacing the base metal; plating stops when the surface of base metal is completely covered, so only a limited coating thickness can be obtained through the immersion process. For both electroless and immersion processes, the intricate chemistry and the control of kinetics are vital to the plating results. The chosen process parameters and chemistry, including pH and chemical ingredients, must be compatible with the solder mask and PCB materials.

5.8.5.2 Metallic systems. Available metallic surface finishes on copper traces include Sn, SnPb alloy, SnNi alloy, Au/Ni, Au/Pd, Pd/Ni, and Pd. The systems containing noble or semi-noble metals, such as Au/Ni, Au/Pd, Pd/Ni, and Pd/Cu, are capable of delivering a coating surface with uniform thickness. Those systems imparting a pure and clean surface also provide a wire-bondable substrate. In addition, wire bonding generally requires a thicker noble metal coating—more than 0.000020 in. A unique feature of the Au/Ni system is its stability under elevated temperature exposure during the assembly process as well as in subsequent service life. When in contact with a molten solder of SnPb, SnAg, or SnBi, surfaces coated with Sn and SnPb are normally associated with a better spreading and lower wetting angle than others. Of the metallic systems, those containing a Ni interlayer are expected to possess a more stable solder joint interface; in these systems, solder is expected to wet on Ni during reflow, because noble metals are readily dissolved in solder. The concentration and distribution of noble metals in solder need to be noted to prevent any adverse effect in solder joining integrity. For a phosphorus-containing plating bath, a balanced concentration of phosphorus in electroless Ni plating is essential. When the P content is too high, wettability suffers; when it is too low, thermal-stress resistance and adhesion strength are sacrificed.

Another characteristic important to solderability is the porosity of the surface. A thinner coating is more prone to porosity-related problems, but the surface density and texture can be controlled by the chemistry and kinetics.

5.8.5.3 Organic coatings. Benzotriazole has been widely recognized as an effective Cu, antitarnish, and antioxidation agent for decades. Its effectiveness, attributable to the formation of benzotriazole complex, is largely limited to ambient temperatures.

As the temperature rises, the protective function disintegrates. Azole derivatives such as imidazole (m.p. 90°C, b.p. 257°C) and benzimidzole (m.p. 170°C, b.p. 360°C) have been used to increase the stability under elevated temperatures. SMT assembly of mixed boards involves three stages of temperature excursion—reflow, adhesive curing, and wave soldering. The reflow step, however, is considered to be potentially the most harmful to the soundness of the organic coating, because it is the step that involves the highest temperature and longest exposure time.

Although the performance of an organic coating varies with the formula and process, the general behavior of organic coating falls within the following regimen:

- There is a need for compatible flux (generally more active flux).
- For mixed boards, there may be a need for more active flux in wave soldering.
- A thicker coating is more resistant to oxidation and temperature but may also demand more active flux.
- An organic coating needs to be employed as the last step of PCB fabrication.
- At temperatures higher than 70°C, the coating may degrade. However, the degradation may or may not affect solderability.
- The coating may be sensitive to PCB the prebaking process (e.g., 125°C for 1 to 24 hr).
- For no-clean chemistry, a N_2 atmosphere or higher solids content may be required in no-clean paste.
- The steam aging test is not applicable.
- It is not suitable for chip-on-board where wire bonding is required.

Nonetheless, when the fluxing activity and process are compatible, an organic coating can be a viable surface finish for PCBs. A bonus effect is that the bare copper appearance of the organic coated surface facilitates the visual inspection of peripheral solder fillets.

5.8.5.4 Comparison of PCB surface finish systems. Whatever its deficiencies may be, HASL provides the most solderable surface. However, comparing a metallic system with HASL, the latter subjects PCBs to higher temperatures (above 200°C), producing inevitable thermal stress in PCBs. Furthermore, HASL is not suitable for wire bonding.

To choose a valid replacement for HASL, many variables need to be assessed. Understanding the fundamentals behind each variable, in conjunction with setting proper priority of importance among these variables for a specific application, is the way to reach the best balanced solution.

When selecting an alternative surface finish for PCB assembly, the key parameters to consider are solderability, ambient stability, high temperature stability, suitable for use as a contact/switch surface, solder-joint integrity, and wire bondability for those assemblies that involve wire bonding, and cost.

Table 5.14 summarizes the relative performance of PCB surface finish systems.

TABLE 5.14 Relative Performance of PCB Surface Finishes

HASL	Au/Ni	Pd/Ni	Pd/Cu	Organic
Pros:				
Most solderable Uniform thickness	Uniform thickness Wire bondable Most stable T	Uniform thickness Wire bondable	Uniform thickness Wire bondable	Uniform thickness Low cost Easy inspection
Cons:				
Nonuniform thickness Potential IMC problem Unsuitable for COB PCB exposed to high temperatures	Higher cost	Higher cost	Higher cost (thicker coating)	Unsuitable for COB Flux and reflow process sensitive High T degradation Cu reaches upper limit in solder bath Required as a last board fabrication step

5.9 Solder-Joint Appearance and Microstructure

5.9.1 Appearance

X-ray, laser thermal, and optical inspection techniques for solder-joint quality assurance have been developed extensively. Visual inspection is commonly used to verify solder-joint quality, and it is still required by military specifications. Thus, a few words are in order about the appearance of solder joints.

The factors affecting the solder-joint appearance, in terms of luster, texture, and intactness, are as follows:

- Inherent alloy luster
- Inherent alloy texture
- Residue characteristics after paste reflow
- Degree of surface oxidation
- Completeness of solder powder coalescence
- Microstructure
- Mechanical disturbance during solidification
- Foreign impurities in the solder
- Phase segregation
- Cooling rate during solidification
- Subsequent heat excursion, including aging, temperature cycling, power cycling, and high-temperature storage

It is known that the process of solidification from melt is crucial to the microstructure development of an alloy, which, in turn, affects its appearance.

Figure 5.49b shows the 63Sn/37Pb off-eutectic microstructure of a two-metal powder mix, and Fig. 5.49a shows the eutectic microstructure of prealloyed powder reflowed under the same conditions. The difference is attributed to insufficient reflow in Fig. 5.49b; its microstructure reflects a slightly duller joint.

Microstructure is also related to alloy strength and failure mechanisms. It is observed that an ideal Sn/Pb eutectic structure, as shown in Fig. 5.49a, imparts a bright and smooth solder surface. Deviation from the eutectic microstructure is normally visualized as a duller joint.

The heating time at melt is another factor. Figure 5.50 shows the microstructure of two 63Sn/37Pb solder joint surfaces made under a regular infrared heating profile (Fig. 5.50a) and with prolonged exposure at peak temperature (Fig. 5.50b). Figure 5.51 shows the cross sections of these two joints; the excessively heated solder joint in Fig. 5.51b appears to be rough on the surface.

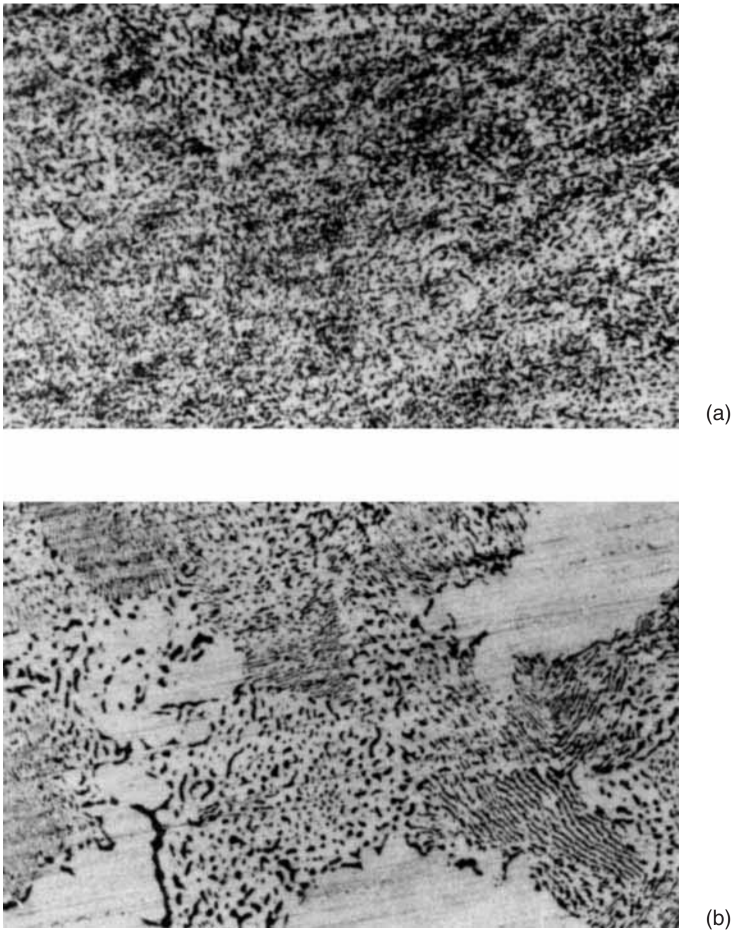


Figure 5.49 SEM micrograph of 63Sn/37Pb structures: *(a)* eutectic and *(b)* off-eutectic.

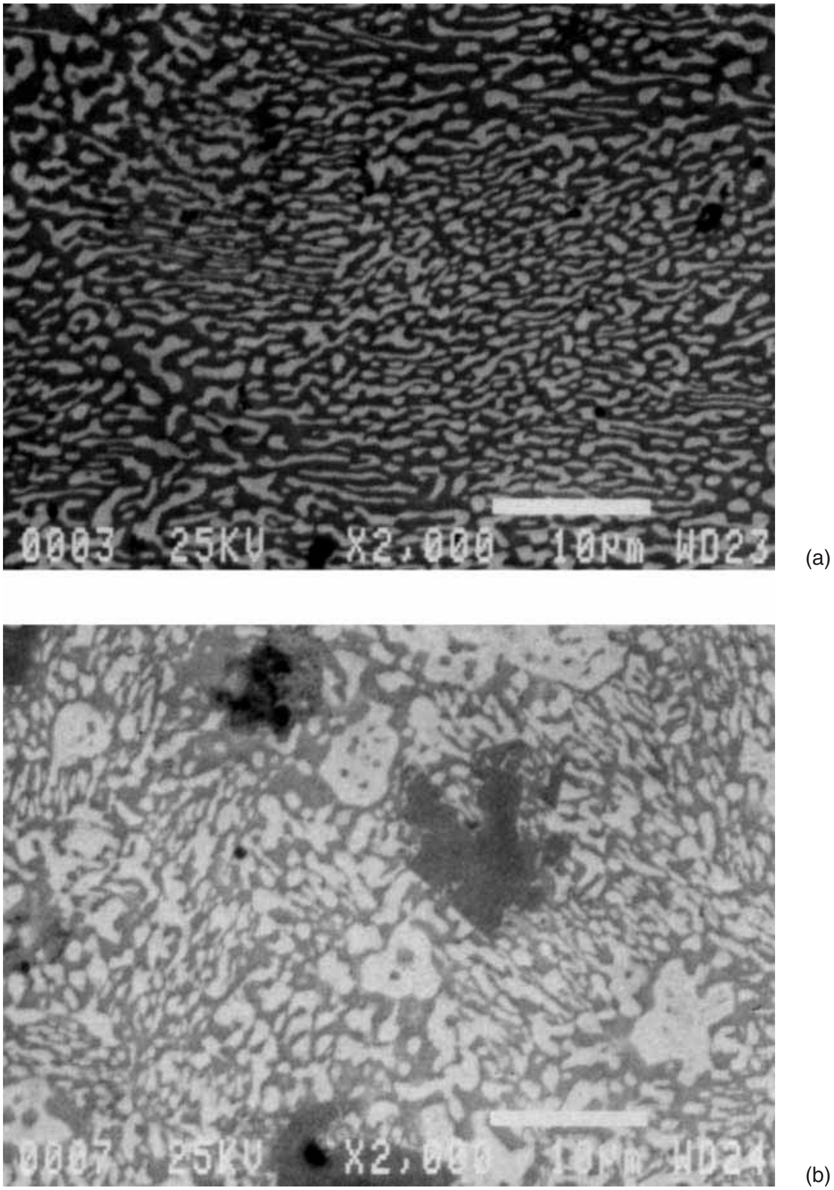


Figure 5.50 SEM micrograph of 63Sn/37Pb solder joint surface reflowed under *(a)* regular and *(b)* prolonged heating.

The residue interference on the molten surface and during its solidification can contribute to a rough texture on the solder surface. Inadequate heating time or temperature will cause incomplete coalescence of solder particles, which also contributes to an unsmooth surface and possibly to an inferior solder joint. During cooling, any mechanical agitation that disrupts the solidifi-

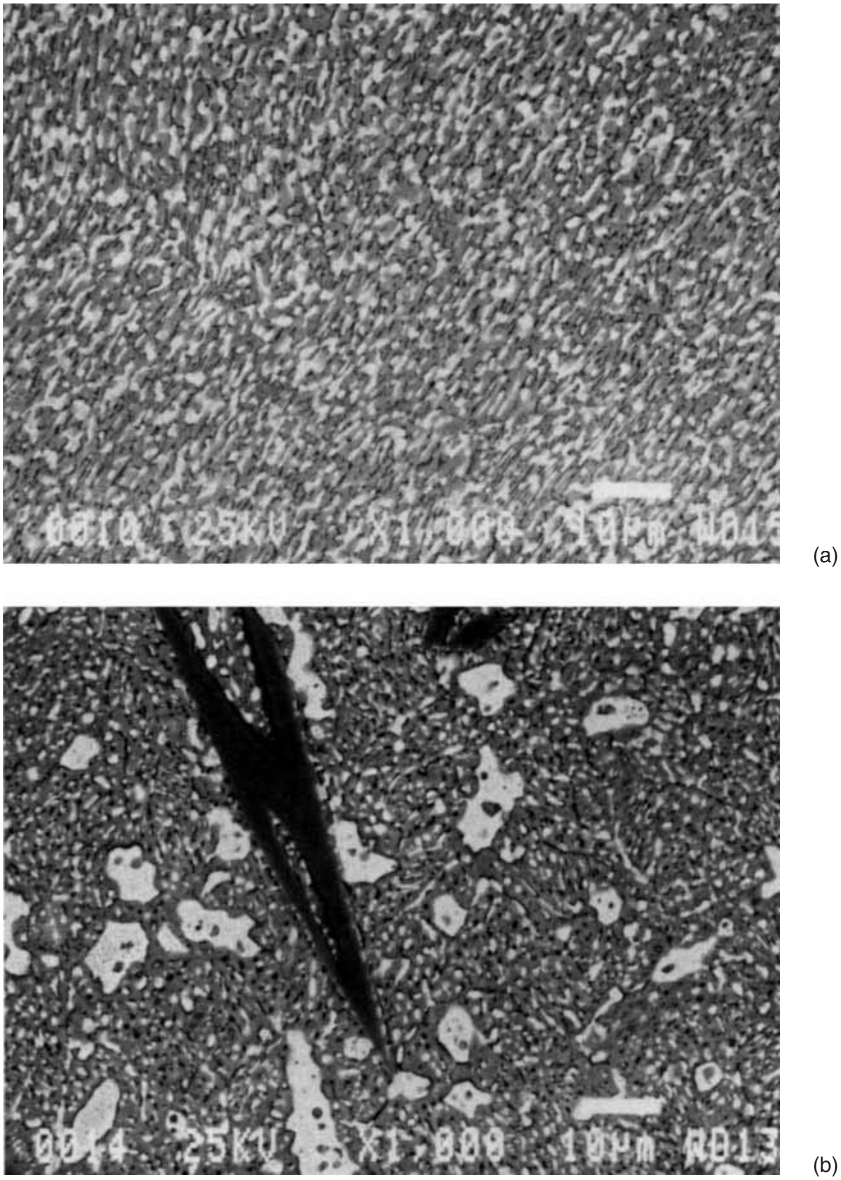


Figure 5.51 SEM micrograph of 63Sn/37Pb solder joint surface cross section reflowed under *(a)* regular and *(b)* prolonged heating.

cation process may lead to uneven solder surface. After the completion of reflow and solidification, heat excursion is expected to have a significant impact on solder-joint appearance, whether it is a surface reaction or internal structure change. Heat excursion can come from different sources, such as high-temperature storage, aging, temperature fluctuation during service, and power cycling during functioning.

In many cases, a duller or a rough joint may not be necessarily defective in a functional sense. Test may confirm that the duller and rougher joints have equivalent mechanical strength. However, one must be prudent in drawing a conclusion regarding joint reliability in relation to joint surface appearance. It should be noted that the surface condition of a metal is considered to be one of the variable that affect its failure mechanism. It should also be noted that the surface appearance may reflect the internal microstructure which, in turn, corresponds to the physical and mechanical properties of the solder joint. In the author's viewpoint, the level of smoothness and brightness that the alloy should show reflect a proper joint having been produced from a proper process.

5.9.2 Microstructure

When dealing with physical objects in the linear dimension larger than 10^2 μm, we work on structure engineering. If we desire to view an object in the scale of 10^{-10} to 10^2 μm, we study material science and nuclear physics. As the scale shrinks to less than 10^{-10} μm, the object becomes intangible and immeasurable. Microstructure essentially falls in the range of 10^{-10} to 10^2 μm. Hence, the understanding of solder joints within this range of dimensions is generally considered adequate for relating material properties to end-use applications.

Solders are normally polycrystallines that consist of an aggregate of many small crystals or grains. Most solder compositions contain multiple, physically distinct metallurgical phases that are formed and distributed according to given thermodynamic and kinetic conditions. For example, 63 Sn/37Pb is typically composed of lead-rich and tin-rich phases in solid state below eutectic temperature. The finer structure with features smaller than grains and phases is called the *submicrostructure*. Macrostructure is coarser than microstructure and is discernible to the human eye.

The parameters affecting the formation of a microstructure during the solder-joint creation process include heating and cooling. For an assembly prone to the formation of intermetallic compounds at the interface or in the intrinsic solder composition, prolonged heating may produce excessive intermetallic compounds at the interface or in the solder joint. When the solder is liquid, intermetallic compounds at the interface may continue to grow and migrate toward the solder joint interior. In extreme cases, intermetallics may emerge onto the free surface of the solder, causing a change in solder joint appearance. As to the cooling effect, the faster its rate, the finer the microstructure becomes. When the cooling rate is slow enough and approaches equilibrium, the microstructure of the eutectic composition normally consists of characteristic lamellar colonies. As the cooling rate increases, the degree of lamellar structure degeneration increases, and colonies eventually disappear. Although it is generally accepted that a faster cooling rate creates a finer grain structure in bulk solder, this rule is often complicated by the interfacial boundary and metallurgical reaction at the interface of solder joints. The nature of the substrate and its metallurgical affinity to solder composition can affect the solder joint Microstructure development. It would not be surprising to see the microstructure of the 63Sn/37Pb joint interfacing with a Ni-plated substrate differ from that of a Cu-plated substrate.

During service life, the integrity of joints made with sound fillet design and good wetting at the interfaces is affected by compatibility between the solder alloy and the substrate metal and subsequent in-circuit and external conditions such as heat dissipation, mechanical load, and environmental temperature fluctuation.

Heat, load, time, and extensive metallurgical interaction between the solder and the substrate metal cause changes in microstructure. Failed solder joints have revealed significant degradation in microstructure that is otherwise hidden in the as-solidified counterpart. In most cases in which the failure is a result of fatigue (fatigue-creep) phenomenon, grain (phase) coarsening has been observed to be a precursor of solder cracks.

If we assess the mechanical properties of a solder joint by using commonly established techniques, then shear strength, creep, isothermal low-cycle fatigue, and thermomechanical creep are the top four parameters. For a eutectic solder composition, the shear strength of the solder joint is improved by a very slow cooling rate, which results in the formation of a near-equilibrium lamellar eutectic structure. On the other hand, strength is also enhanced by using a very fast cooling rate, which produces grain size refinement. For plastic deformation under creep mode, creep resistance depends on the operating mechanism. When the lattice or vacancy diffusion process is predominating step, creep resistance is often lower, with a finer microstructure. This is the result of an increased vacancy concentration created by a faster cooling rate. Under an isothermal fatigue environment, the relationship between microstructure and fatigue resistance is more complex. Nonetheless, microstructure homogeneity is more important to low-cycle fatigue resistance. Thermal cycling fatigue resistance is often associated with decreased grain size.

To examine microstructural features, a 100 to 5000× magnification is needed. The characterization can utilize optical (light) or electron microscopy or, preferably, both.

For light microscopy, the solder specimen must be carefully prepared through metallagraphic techniques involving successive grinding and polishing. The technique uses ascending levels of abrasive particle fineness bonded on papers or used as slurry on a cloth-covered wheel. The size of the abrasive particles can range from 23 μm to submicrometer size. Then, the specimen goes through an etching process. In comparison, scanning electron microscopy (SEM) requires little sample preparation when the sectioning (cutting) of the specimen is properly performed. Images from either secondary or backscattered electron signals can be readily obtained. Either provides informative characteristics with distinctive features. By combining information from both images, the microstructure and morphology of a solder joint can be better understood.

For solder joints, the two most information-revealing parameters are elemental composition and microstructure. For a given solder composition, the microstructure in the form of a quality microgram provides “sights” and “insights” into state of solder-joint integrity.

5.10 Solder-Joint Integrity

Solder-joint integrity can be affected by the intrinsic nature of the solder alloy, the substrates in relation to the solder alloy, the joint design or structure, the joint-making process, and the external environment to which the solder joint is exposed. Therefore, to assure the integrity of a solder joint, a step-by-step evaluation of the following items is warranted:

- Suitability of solder alloy for mechanical properties
- Suitability of solder alloy for substrate compatibility
- Adequacy of solder wetting on substrates
- Design of joint configuration in shape, thickness, and fillet area
- Optimal reflow method and reflow process in terms of temperature, heating time, and cooling rate
- Conditions of storage in relation to the aging effect on the solder joint
- Conditions of actual service in terms of upper temperature, lower temperature, temperature cycling, vibration, and other mechanical stress
- Performance requirements under the conditions of actual service
- Design of viable accelerated testing conditions that correlate with actual service conditions

5.10.1 Basic failure processes

In the real world, solder-joint failure often occurs in complex mechanisms involving the interaction of more than one basic failure process. Although creep-fatigue is considered to be a prevalent mechanism leading to the eventual solder joint failure, separate test schemes in creep and fatigue are often conducted to facilitate data interpretation and an understanding of the material behavior. The basic processes or factors that are believed to contribute to solder failure during service are as follows:[1]

- Inferior or inadequate mechanical strengths
- Creep
- Mechanical fatigue
- Thermal fatigue
- Intrinsic thermal expansion anisotropy
- Corrosion-enhanced fatigue
- Intermetallic compound formation
- Detrimental microstructure development
- Voids
- Electromigration
- Leaching

5.10.2 Reliability of BGA solder interconnections

By virtue of array packages' attributes, BGA interconnections on the mother board generally consist of a relatively high number of solder joints per device in comparison with SOICs, PLCCs, and QFPs. The higher number constitutes a higher probability of defect occurrence. This, coupled with less accessibility for inspection, rework, and repair, makes the consistency of forming array interconnections and their quality and integrity critically important.

The main concern for the reliability of array interconnections stems from two areas. First, array solder interconnections are less compliant than conventional peripheral-leaded interconnections. The decreased compliance may contribute to reduced performance under a fatigue environment because of the cyclic thermal stress and strain imposed on the system by temperature fluctuation and in-circuit power on/off. The surface mount array interconnection is also relatively new, and its applications are still in the infant stage for board-level assembly. Statistically substantiated data are lacking in terms of field performance. A common failure mode of PBGA on PCB interconnection is shown in Fig. 5.52. Factors affecting long-term reliability of array solder joints are described below.

Component package. The temperature profile to which each solder joint is exposed is a major contributor to the distribution of thermal stress and strain among array solder joints. In addition to the external temperature change, the temperature profile depends on the functional characteristics of the die, the

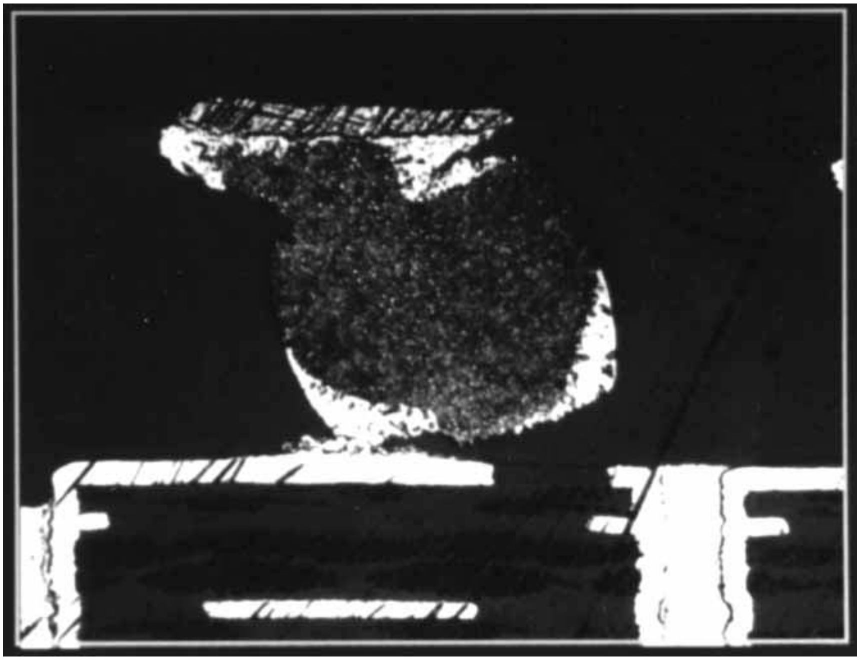


Figure 5.52 A common failure mode of PBGA on PCB interconnection.

ratio of die to package size, the thermal property of the carrier substrate, and power dissipation. A study of IC packages ranging from 81 to 421 pins under power cycling demonstrated that outermost solder joints reached 84.3°C while center joints were 98.9°C (1.2°C) below the junction temperature for an 81-pin package.

However, the 421-pin package, having a lower die-to-package size ratio, experienced a large temperature differential between the outer joints (56.2°C) and the center joints (98.5°C).[20] It was found that a 165-pin device that had the largest die size of the components under study had the earliest failure, and its cycle-to-failure was lower than that of the 225-pin device.

It was also found that the solder joints directly underneath the perimeters of the die failed first under temperature cycling. This indicates that solder-joint fatigue life depends more on die size than package size, and the relative location of solder joints to the edge of the die plays an important role in the fatigue performance of solder joints.

Board materials. The two characteristics of board materials that have the most influence on the long-term performance of solder interconnections are planarity and coefficient of thermal expansion (CTE). Poor board planarity adds to the coplanarity problem of the BGA package, contributing to the occurrence of solder joint distortion, which in turn may lead to early failure of the solder joint under cyclic stresses. The CTE of conventional board material (FR-4) is approximately 15×10^{-6}/°C, while the ceramic carrier substrate of CBGA has nominal CTE of 6 to 7×10^{-6}/°C. The CTE of solder material falls in the range of 21 to 30×10^{-6}/°C, depending on the alloy. The differential in CTE between the board and carrier substrate results in an additional force of cyclic plastic deformation in solder joints under temperature-imposed conditions. Closely matching the board and carrier substrate CTE reduces thermally induced stresses.

Solder composition. The solder composition of the BGA carrier solder bumps affects the mechanical behavior of the solder interconnections. In general, a solder that is "stronger" in fatigue and creep resistance is expected to deliver a better service life. The thickness (height) of solder joints between the BGA and board is much larger than that of a fine-pitch QFP. The actual BGA solder joint height depends on the diameter of the bumps and the dimensions of solder pads; for example, the 0.022-in (0.55-mm) BGA solder height compares with a 0.003-in (0.08-mm) height for the QFP. Because the solder height for BGAs is larger, the effect of the intrinsic properties of BGA solder material is expected to be more pronounced than for QFPs.

Solder joint configuration and volume. The shape and configuration of solder joints can change the stress distribution and consequently affect failure mode development. Solder joint volume contributes to the kinetics of solder joint crack propagation. In addition, uniformity and consistency in volume and configuration among array solder joints within a package are important.

Other material: underfill. Several studies have demonstrated that an epoxy that fills the air gap between the solder and the underside of the component is beneficial to the fatigue life of the solder joints. For plastic BGAs, the fatigue life of solder joints for over molded pad array carriers (OMPACs) under temperature cycles of –40 to 125°C improved nearly two-fold with epoxy underfill.[20] The underfill around the chip and the solder of the SLICC (slightly larger than IC carrier) assembly, which is a combination of flip-chip and ball array technology, was used to enhance solder joint reliability.[20] The eventual solder joint failure under thermal shock of –55 to 125°C was attributed to the separation of the underfill from the die surface. This loss of adhesion was further related to foreign contamination that was not thoroughly removed during the cleaning procedure.

A similar enhancement in solder joint performance by means of epoxy underfill was observed for the assembly of ceramic BGAs.

Manufacturing process. The above-described factors contribute to the long-term performance of solder joints during their service life. However, the ability to make high-quality solder joints at the point of production is equally important. Although an existing installed surface mount operation can be directly used to mount BGAs on a mother board, the setup of process parameters (particularly reflow temperature profile), control of the process, and proper ambient conditions are keys to making quality solder joints. High humidity and high temperature are generally detrimental to surface mount manufacturing.

Material behavior—in relation to temperature change, component effect, and design—is a significant factor in the reliability of interconnections. Understanding each of these areas in conjunction with establishing a quality manufacturing process is the means to full utilization of the merits of BGA packages.

5.10.3 Reliability of peripheral solder joints—component lead effect[20]

Consistency among components in their intended lead dimensions and consistency among the leads of a single component are crucial to the quality of solder joints and to the overall yield of manufacturing surface mount assemblies. Although specifications for lead dimensions exist, deviations from these specifications and variations within the specifications in commercial component suppliers often contribute to manufacturing problems in terms of quality and yield. This is because physical characteristics affect the long-term performance of solder joints. The effect can come from various sources as listed below:

- Lead material
- Lead length
- Lead width
- Lead thickness
- Lead height
- Lead co-planity
- Lead material

Common lead materials include copper, Alloy-42, and Kovar. Lead stiffness varies with the design of the component package; however, the intrinsic stiffness follows the general order of

copper < Kovar < Alloy-42

It is believed that less stiff or more compliant lead materials are more favorable to the fatigue life of solder joints, other conditions being equal.

- *Lead length.* For QFPs, the lead length is measured from the toe to the contact point with the package body in a horizontal direction. The fatigue life of solder joints was found to increase by 67 percent as the lead length was increased from 0.085 in (2.13 mm) to 0.1125 in (2.82 mm).[21]
- *Lead width.* Figure 5.53 shows the effects of lead width on solder joint fatigue life;[21] fatigue life decreases as lead width increases. It was found that fatigue life is more sensitive to lead thickness than to lead width. The fatigue life drops rapidly as lead thickness increases, as shown in Fig. 5.54.
- *Lead height.* Figure 5.55 shows the effect of lead height as measured from the contact point of lead and package body to the solder pad in a vertical direction. As can be seen, solder fatigue life increases with increasing lead height.
- *Co-planarity.* Production defects are often related to the co-planarity of component leads, which includes starved solder joints and open joints. To avoid problems caused by poor co-planarity, it is advisable to maintain lead co-planarity in the range of 0.002 in (0.05 mm) for fine-pitch components, although 0.004 in (0.1 mm) seems to be an industry-accepted value, and

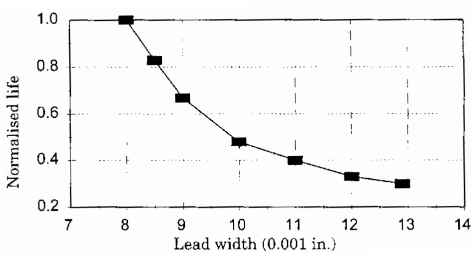


Figure 5.53 Solder joint fatigue life vs. QFP lead width.

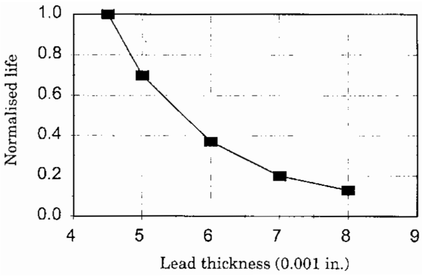


Figure 5.54 Solder joint fatigue life vs. QFP lead thickness.

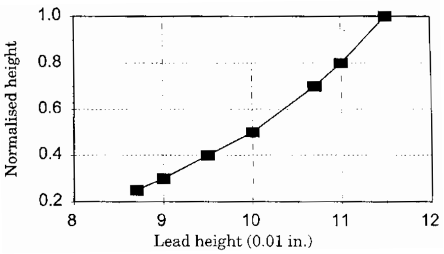


Figure 5.55 Solder joint fatigue life vs. QFP lead height.

0.003 in (0.075 mm) for fine-pitch devices. JEDEC 95 specifies co-planarity for individual components.

5.10.4 Challenges in modeling solder joint life prediction

It is well recognized that solder joint reliability relies not only on intrinsic material properties but also on design, component type, the process that produces solder connections, and the long-term service conditions. As electronic IC packages and components continue to change at a rapid pace, it is highly desirable to have a model able to predict the service life and reliably of solder joints under a specific set of conditions. However, to derive such a model is an ever-daunting task. This is primarily because of the complex nature of solder materials in conjunction with the “active” service conditions. Solder materials display a more complex behavior in response to temperature, stress, and time than do high-temperature materials such as steel. Much remains to be understood. The challenges are further complicated by the high level of versatility in circuit boards in terms of various materials and designs.

For a given solder composition and design, the main physical factors affecting the solder material performance are temperature, ambient environment, strain range, strain rate, loading wave form, intrinsic microscopic structure, and surface condition of the materials. Furthermore, the solder joint is expected to behave differently from bulk solder materials. Hence, some established mechanical and thermal behavior of solders may not be applicable. This is presumably a result of the following causes:

- The presence of high ratio of substrate surface to solder volume, resulting in a large number of heterogeneous nucleation sites during solidification
- A concentration gradient of elemental or metallurgical composition when the solder joint is formed

Either of the above conditions may lead to a structure that is not homogeneous. As solder joint thickness decreases, the interfacial effect is more pronounced. Accordingly, the properties of solder joints may be altered, and the failure mechanism may be incongruent with that derived for bulk solder. It is generally accepted that, under cyclic strain conditions, the creep-fatigue process essentially accounts for the solder joint degradation, assuming that the interface problems, such as those caused by excessive intermetallics or poor wetting, are not the determining factors for failure. Consequently, most studies have been carried out under creep-fatigue testing mode. The goals in studying the creep-fatigue process are as follows:

- One needs to understand material behavior under cyclic strains, which one inevitably encounters during solder joint service life in electronic assembly.
- One also needs to develop or improve the resistance to degradation under cyclic strains by taking a system approach.
- It is also important to predict the fatigue life of solder joints so that performance reliability at a given set of service conditions can be designed and assured.

Many fatigue life prediction methods have been proposed, including the frequency-modified Coffin-Manson (C-M) method, strain range partitioning, fracture mechanics, and finite element analysis (FEA). The methodologies are largely borrowed from the established fatigue and creep phenomena of steels as a result of extensive studies coupled with the field data obtained over a longer period of time. Both the frequency-modified C-M method and fracture-mechanics-based methods are not capable of handling a complex loading wave form, although fracture mechanics can monitor the effect of interfacial crack initiation and propagation on life in a comprehensive manner, and the frequency-modified C-M method takes frequency effect into consideration. Strain range partitioning is able to deal with the strains in any wave form, yet separating the total inelastic strain range per cycle into creep strain and plastic strain is not easy. FEA also lacks the capability of including complex wave forms. Increased efforts in tailoring the basic life predication models established for steels are burgeoning in electronics industry. Although these efforts may have generated models that apply to solder joints in comparative sense, a true working model has yet to be found.

Service conditions under which solder joints must perform in electronic packages and assemblies often involve random multiaxial stresses, which expose solder joints to creep range in addition to cyclic strains. At this time, sufficient and integrated data regarding solder joint behavior under such conditions, and corresponding damage evolution, are much lacking. Consequently, some important areas and conditions are grossly ignored in the modeling scheme. Listed below are the areas that either have not been included or not adequately covered. They are in turn considered to be the reasons that contribute to the limitations of the existing models to the real-world applications.

1. Effect of initial microstructure
2. Effect of grain size
3. Effect of microstructure that is not homogeneous
4. Change in microstructure versus external conditions
5. Multiaxial creep-fatigue

6. Identification of the presence or absence of crack-free materials at the starting point
7. Size of existing cracks, if present
8. Effect of interfacial metallurgical interaction
9. Joint thickness versus interfacial effect
10. Damage mechanism—transgranular or intergranular
11. Potential damage mechanism shift (from transgranular or intergranular)
12. Presence or absence of grain boundary cavitation
13. Effect of fillet geometry
14. Effect of free surface condition
15. Correlation of accelerated testing conditions with the actual service condition
16. Testing condition versus damage mechanism
17. Service conditioned to include possible variation in chip-power dissipation over time
18. Ambient temperature change
19. The number of on/off power cycles
20. Effect of variation in co-planarity among solder joints

Including the above-listed areas in modeling is not only overwhelmingly time consuming but also extremely difficult. It is a challenge indeed. However, the inclusion of all the above areas in devising a model is necessary to achieve a model's ultimate utility that predicts service life solder joints for a specific application. Until a universal model is validated, a practical system must be created using a combination of existing and experimental data.

5.10.5 Creep and fatigue interaction

Serving as interconnections in electronics packaging and assembly, solder materials usually entail simultaneous exposure to more than one hostile environment, such as temperature. Most solder materials, even under ambient temperature (298 K), reach homologous temperatures (T/Tm) well beyond 0.5. Under these service conditions, both creep and fatigue processes may exist and operate interactively. These situations would be equivalent to creep under cyclic loading or fatigue at high temperature.

Whether a "wear-out" phenomenon should be viewed as creep-aggravated fatigue or fatigue-accelerated creep depends on several factors. Generally, when the cyclic stress (or strain) amplitude is small in comparison with the mean stress (or strain), or the applied frequency is low and/or the temperature is high, the phenomenon can be treated as creep perturbed by fatigue. In contrast, when the cyclic stress amplitude is large, or the applied frequency is high and/or the temperature is low, the degradation phenomenon should be considered fatigue accelerated by creep behavior.

Solder material in electronic interconnections may undergo changes through one of the two interactive behaviors involving both creep and fatigue. The material properties for obtaining maximum creep resistance often differ from those for maximum fatigue resistance. The development of improved materials should be aimed at enhancing both creep and fatigue resistance.

5.11 Lead-Free Solders

The issue of lead in electronics has gone through more than 12 years of deliberation and debate by legislative bodies, manufacturers, and individuals around the world. Various ideas have been exhibited, particularly in U.S., and individual opinions expressed by both supporters and oppositions have been eloquent. On the global landscape, the tangible progress in technology and legislation differs in the three major continents—North America, the European Union, and Asia. Although a uniform consensus is still to be worked out, the technology has advanced, the business climate has changed, and, overall, the marketplace is striding into a highly environmentally-conscious playing field.

Various organizations have made dedicated effort to inform the industry about this pivotal issue. For instance, the Swedish Institute of Production Engineering Research (IVF) has developed the "Electronics Design-for-Environment Webguide," which disseminates updated information to the industry regarding the development of legislation and technology. The International Tin Research Institute (ITRI) launched the Lead-Free Soldering Technology Centre, and IPC initiated the Lead Free Forum on the Internet. Professional organizations such as Surface Mount Technology Association (SMTA) and International Microelectronics and Packaging Society (IMAPS) have organized symposia dedicated to disseminating knowledge and information.

Global legislations in the three regions are described separately, below.

To producers and manufacturers, waste reduction, recovery, and recycling should be and inevitably will be treated as a long-term goal supported by an ongoing effort. A product should be designed for minimal environmental impact and with the full life cycle in mind. Life-cycle assessment includes all the energy and resource inputs to a product, the associated wastes, and the resulting health and ecological burdens. Overall the goal is to reduce environmental impacts from cradle to grave.

5.11.1 Status of worldwide legislation

5.11.1.1 United States. The Lead Exposure Reduction Act (S.391) was introduced in 1991, putting restrictions on lead solder, banning some and limiting lead content in others to less than 0.1 percent. In April, 1993, a sister bill

(S.729) to the Lead Exposure Reduction Act emerged. Under this Act, in addition to banning lead solders for plumbing, an inventory and concern list, new use notification requests, and product labeling were included. The EPA must inventory all lead-containing products and then develop a "concern list" of all products that may reasonably to be anticipated to present an unreasonable risk of injury to human health or the environment. Any person can petition the EPA at any time to add a product to the "concern list." Anyone who manufactures or imports a lead-containing product that is not on the inventory list must submit a notification to the EPA. The products on the "concern list" must be labeled.

On May 25, 1994, the Lead Exposure Reduction Act (S.729) passed the Senate floor. Furthermore, the Lead Tax Act (HR 2479 and S. 1357) was also introduced in June, 1993, placing a $0.45 per pound tax on all lead smelted in the United States and on the lead content of all imported products.

The Resource Conservation and Recovery Act (RCRA) classifies solder skimmings and solder pot dumpings as scrap metal, not as hazardous waste, if can be shown that they are recycled. However, if they are disposed of as a waste, they must pass the Toxic Characteristic Leaching Procedure (TCLP) test with the established maximum concentration of lead by TCLP testing being 5 ppm; solder skimming and pot dumpings are expected to fail. Therefore, they are not exempted from RCRA hazardous waste regulations.

Waste solder materials are not considered hazardous if they are returned to a reclaimer or the supplier. A container with less than 3 percent by weight of its total content is considered empty and is not subject to hazardous waste regulation.

In 2001, the U.S. EPA tightened Toxics Release Inventory reporting requirement by reducing the reporting threshold for lead and lead compounds from 25,000 lb for manufacturing and processing (10,000 lb for other use) to 100 lb. This new EPA regulations under the Toxic Release Inventory (TRI) program requires all facilities that manufacture, process, or otherwise use 100 lb of lead or lead compounds to report their TRI lead releases annually, beginning July 1, 2002. The 100-lb lead threshold is approximately 270 lb of typical electronic solder based on 63Sn37Pb alloy. The new TRI lead rule mandates that releases be reported to within 0.1 lb, which is only 1.6 oz or 45.3 g. This is an extremely small amount over a one-year period, creating great demands on facilities as they calculate their annual lead releases.

5.11.1.2 Japan. The newly enacted legislation Home Electronics Recycle Law mandates the recovery of lead used in home electronics. Prompted by this law and the guidelines from the Japanese EPA and government to reduce lead and increase recycling, many Japanese electronic companies have announced voluntary plans to reduce or eliminate the use of lead in solder.

Some companies have implemented lead-free solders in commercial products. For example, Hitachi, Matsushita (Panasonic), and NEC announced intentions to reduce lead use to 50 percent of 1997 level by year 2002, and to stop using lead-containing solder in 2003.

Most companies, including Sony, Toshiba, NEC, Hitachi, and Matsushita, have their own programs for developing or selecting a suitable lead-free alloy composition.

5.11.1.3 Europe. Among the European Commission proposals, two main directives applicable to this industry are

- *WEEE.* Waste Electrical and Electronic Equipment Directive
- *RoHS.* The Restriction of Use of Hazardous Substances Directive

The European Commission Directive proposed implementation of WEEE by 2006 (2005).

According to the proposed document, WEEE stipulates "…components containing lead will have to be removed from any end-of-life electrical and electronic equipment (EEE) that is destined for a landfill, incineration or recovery…," where EEE was defined as equipment dependent on electric currents or electromagnetic fields to work properly, as well as equipment designed for use with a voltage rating not exceeding 1,000 V for AC and 1,500 V for DC.

The purpose of the WEEE Directive is, as a first priority, the prevention of waste electrical and electronic equipment and in the addition, reuse, recycling, and other forms of recovery of such wastes so as to reduce waste disposal of waste. It also seeks to improve the environmental performance of all economic operators involved in the life cycle of electrical and electronic equipment and in particular operators directly involved in the treatment of waste electrical and electronic equipment

The purpose of the RoHS Directive is to approximate the laws of the Member States in terms of restrictions on the use of hazardous substances in electrical and electronic equipment, and to contribute to the environmentally sound recovery and disposal of waste electrical and electronic equipment.

RoHS Prevention includes

- Lead
- Mercury
- Cadmium
- Hexavalent chromium
- Polybrominated biphenyls (PBB)
- Polybrominated diphenyl ether (PBDE)

In 1994, Nordic Ministers of Environment stated "…in the long run the phaseout of lead is necessary to reduce risk from lead exposure on human health and the environment.…"

5.11.1.4 Examples of implementation. The legislative thrust in Europe and Japan is moving the industry toward "green manufacturing" and environmentally conscious workplaces. An exemplary lead-free manufacturing process has been employed successfully to produce the Panasonic-Matsushita minidisk player models. It was reported by the manufacturer that the production enjoyed a relatively low melting point of 210°C while offering the same workability, and quality and reliability in the finished product is similar to that achieved with 63Sn/37Pb.

Figure 5.56 exhibits the main circuit card of the Panasonic MR100, which evolved from player types (MJ30, MJ70) to this player/recorder. The main cards for all three products were produced in lead-free manufacturing with Sn/Ag/Bi/Cu alloy compositions.

5.11.2 Technology and approaches

Looking back to approximately 12 years ago, when the industry started to "seriously" explore and conduct research in lead-free solders for making electronic products, this author indicated that any viable lead-free solders intended to replace Sn/Pb eutectic or near-eutectic compositions could not escape from being an Sn-based system (i.e., a minimum of 60 wt percent of tin).

This conclusion was based on both fundamental and practical perspectives. Fundamentals include metallurgical bonding capability on commonly used substrates, dynamic wetting ability during reflow process, and metallurgical "interactions" or alloying phenomena between elements. Practical factors include the availability of natural resources, manufacturability, toxicity, and cost.

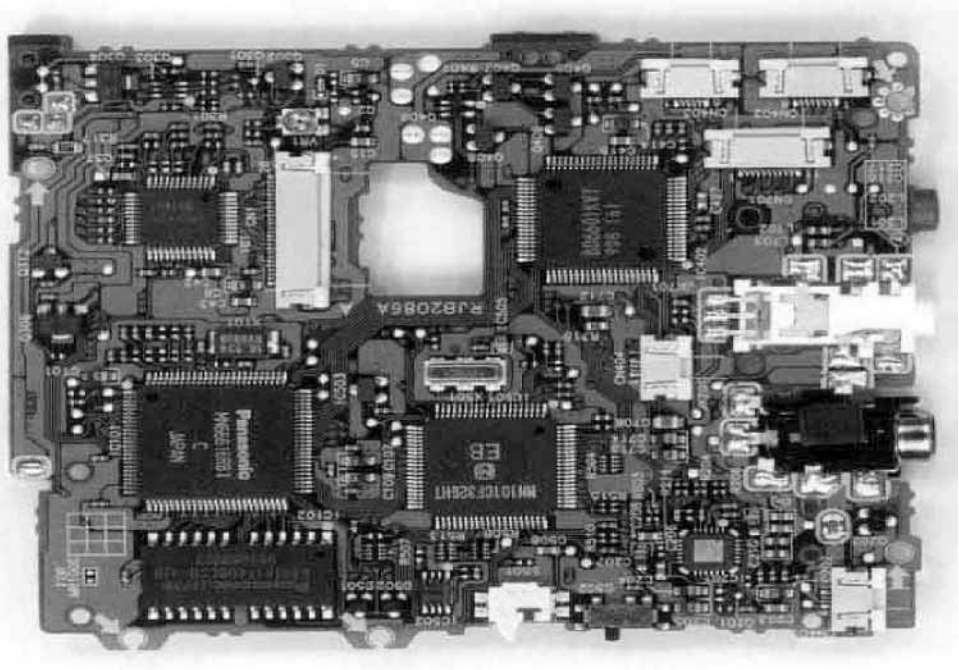


Figure 5.56 Main circuit card of Panasonic minidisk player MR100.

My another query back then was, “What constitutes futuristic solders?”[22] Is the environmentally friendly and failure-free solder joint technology a utopia or ultimately achievable performance? Solder alloys of Sn/Pb eutectic, along with near-eutectic or containing 2 percent Ag, have successfully served the function of making mechanical, electrical, and thermal connections for decades. However, the operating temperature (above room temperature) of electronic products is well above the “homologous” temperature. Based on the material principle, even at the ambient operating temperature, it is the highest application temperature that any engineering materials have ever endured. It thus comes as no surprise that local fatigue micro-cracking and global creep micro-cracking can occur in solder joints during their service life.

It is reasonably well substantiated that the common thermal fatigue failure is linked with the Pb-rich phase. It is therefore expected that the absence of Pb-phase in a properly designed lead-free tin-based solder may impart improved mechanical behavior, resulting in strengthened solders. With increased requirements on the integrity and reliability of interconnections in electronic and microelectronic assemblies, a better solder should always find its useful place.

The two crucial material characteristics for selecting the constituent elements and their specific dosages in the design of lead-free solders are (a) the elements’ ability to alloy with Sn and (b) their melting point lowering properties while alloying with Sn.

Based on metallurgy, elements such as In, Bi, Mg, Ag, Cu, Al, Ga, and Zn are the candidates that can lower the melting temperature of Sn to create Sn-based alloys that possess the required properties for electronic packaging and assembly. Table 5.15 tabulates the speculative melting point reduction with Sn at the selected temperature ranges for the candidate elements.[30]

TABLE 5.15 Estimated Melting Temperature Reduction of Sn by the Selected Elements at the Specified Temperature Ranges

	Melting temperature reduction		
Element	160 to 183°C	183 to 199°C	200 to 230°C
In	2.3	2.1	1.8
Bi	1.7	1.7	1.7
Mg	–	–	16.0
Ag	–	–	3.1
Cu	–	–	7.1
Al	–	-	7.4
Ga	2.6	2.5	2.4
Zn	–	3.8	3.8

5.11.2.1 Alloy strengthening principles. From a material point of view, the crystalline alloys can deform via one or a combination of the following mechanisms:

1. Slip
2. Dislocation climb
3. Shear on grain boundary
4. In-grain vacancy or atomic diffusion

It is generally understood that fatigue failure and material cracking is often caused by dislocation slip and the localization of plastic deformation. It is also generally understood that plastic deformation kinetics follows the power-law dislocation climb-controlling mechanism under high-stress/low-temperature conditions. In a low-stress region at high temperature, the grain boundary sliding becomes a rate-controlling process. Therefore, to strengthen the performance of conventional solders that are subject to stressful conditions as a result of external temperature fluctuation and/or-in-circuit power dissipation and power on-off electronic circuit boards, several approaches, as listed below, can be considered.

5.11.2.2 Strengthening approaches. Under high-temperature conditions (above room temperature) to which solder joints are normally exposed, the mobility of atoms increases, and so do dislocations. Other crystallinic defects such as vacancies also increase. Additional slip systems are introduced, and metallurgical stability is unfavorably affected. In addition, environmental effects (oxidation, corrosion) become more pronounced.

Approaches that can potentially hinder the above material phenomena are expected to enhance the performance of solders, which in turn will achieve the performance levels required for new and future applications. Such approaches include

1. Microscopic incorporation of nonalloying dopant
2. Microstructural strengthening
3. Alloy strengthening
4. Macroscopic blend of selected fillers

These approaches involve both process and material factors.[23–27] For example, solid solutioning where solute atoms normally reduce the stacking fault energy and favorably control the diffusion behavior is one widely adopted strengthening mechanism. In any of these approaches, the objective of the alloy design is to set the proper parameters to achieve the following properties:

- Phase transition temperatures (liquidus and solidus temperature) as close to Pb bearing counterparts as practical

- Suitable physical properties—specifically, electrical and thermal conductivity and thermal expansion coefficient
- Metallurgical properties that are compatible with the interfacial substrates of components and boards
- Adequate mechanical properties, include shear strength, creep resistance, isothermal fatigue resistance, thermomechanical fatigue resistance, and microstructural stability
- Intrinsic wetting ability
- Environmental shelf stability
- Relatively low (or no) toxicity

5.11.2.3 Alloy design. For a Sn-matrix, candidates that can serve as viable alloying elements are quite small in number, practically limited to Ag, Bi, Cu. In, and Sb. However, doping elements may extend to a larger group of elements and compounds. Metallurgical interactions (reactions) and microstructure evolution in relation to temperature rise provide the critical scientific basis for developing new lead-free solders.

Binary phase diagrams provide general information about the conditions and extent of metallurgical interactions, although complete phase diagrams beyond the binary system are scarce. Nonetheless, binary phase diagrams offer a useful starting point.

After a decade of research, we found that the actual test results of the designed multiple-element alloy compositions came very close to the anticipated features in terms of properties and performance between a candidate element and Sn-matrix.[24–28]

To illustrate the point, as examples, Se and Te were found to readily embrittle the Sn-based alloys. Sb in an improper amount quickly jeopardizes the alloy's wetting ability. The distribution of In atoms in the Sn host lattice is sensitively reflected in the fatigue performance. An improper dosage of Bi may result in Bi second-phase precipitation, which can render the solder extremely brittle. The formation of intermediate phases and intermetallic compounds between Sn and Cu, Ag, or Sb, remarkably affect the strength and fatigue life of the alloy, which in turn depends on the concentration of each element as well as on the relative concentration among the elements.

The general performance is as predictable as stated, but a high-performance alloy composition demands a stunningly intricate balance of the elemental constituents. In each of compositional system, the useful products are often a specific composition or a narrow range of compositions at best.[32–34] Over the past decade, many compositions have been developed and disclosed. More than 75 patents on lead-free solder alloys have been issued worldwide. Among them, most compositions made public are not ready to be used in commercial applications. However, lead-free alloys exist that can be put to use, delivering desirable performance that is superior to that of their lead-containing counterparts.

New solder alloys must possess the characteristics that are compatible with the practical manufacturing techniques and end-use environment. The basic material properties such as liquidus/solidus temperature, electrical/thermal conductivity, intrinsic wetting ability on surfaces that are commonly used, mechanical properties, and environmental shelf stability, must be gauged. Under the current framework, conductivity and shelf stability are not as sensitive to the makeup of a specific system as intrinsic wetting ability, mechanical performance, and phase transition temperatures. Ability to optimize these properties through in-depth application of materials science and metallurgical phenomena is the key.

5.11.3 Pb-free solder vs. Pb-bearing solder[29–31]

The driving forces behind the lead free solders are primarily performance demands and environmental/health concerns. It is reasonably well substantiated that common thermal fatigue failure for solder interconnections is linked to the Pb-rich phase. This Pb-rich phase cannot be effectively strengthened by Sn solute atoms because of limited solubility and Sn precipitation. At room temperature, the limited solubility of Pb in an Sn matrix renders it incapable of improving the plastic deformation slip. Under temperature cycling (thermomechanical fatigue) conditions, this Pb-rich phase tends to coarsen and eventually leads to the solder joint crack. It is therefore expected that the absence of Pb-phase in a properly designed lead-free tin-based solder may impart improved mechanical behavior, resulting in strengthened solders. The new alloys selected and listed below manifest improved performance over 63Sn/37Pb.

On the international landscape, some companies have implemented lead-free solders in commercial products. Many manufacturers have initiated their own programs for developing or selecting a suitable lead-free alloy composition.

5.11.4 Solder alloy selection—general criteria

Generally, the alloy selection is based on the following criteria:

- Alloy melting range in relation to service temperature
- Mechanical properties of the alloy in relation to service conditions
- Metallurgical compatibility, consideration of leaching phenomenon, and the potential formation of intermetallic compounds
- Rate of intermetallic formation in relation to service temperature
- Other service compatibility (considerations such as silver migration)
- Wettability on specified substrate
- Eutectic versus noneutectic compositions
- Ambient environment stability

5.11.5 Selection menu—Pb-free solder[30]

From the simplest alloy (a binary system) to incrementally complex systems containing more than two elements, lead-free materials have been thoroughly explored, designed and studied.[30,32–34] Six systems and their corresponding compositions stand out in terms of their performance merits. Their strengths in comparison with the established alloy compositions are summarized below. These six systems are

1. Sn/Ag/Bi
2. Sn/Ag/Cu
3. Sn/Ag/Cu/Bi
4. Sn/Ag/Bi/In
5. Sn/Ag/Cu/In
6. Sn/Cu/In/Ga

A detailed discussion of each of these systems is omitted in this text. Readers can obtain detailed illustrations and data for each of these systems in a newly released textbook.[30] Some compositions are covered by patents.[32–42] The selected compositions from each of the systems are also compared with the pertinent known lead-free alloys as well as with 63Sn/37Pb. Figures 5.57 through 5.66 summarize the relative performance of these selected compositions with the established solder alloys. An overall comparison is provided among these six systems, leading to the ranking by melting temperature (Table 5.16) and fatigue life (Table 5.17), respectively, and to a final slate of selections.

TABLE 5.16 Ranking of Viable Alloy Compositions by Melting Temperature

Alloy	Melting T°C	N_f
8.52Sn/4.1Ag/2.2Bi/0.5Cu/8.0In	193–199	10,000–12,000
88.5Sn/3.0Ag/0,5Cu/8.0In	195–201	>19,000
93.3Sn/3.1Ag/3.1Bi/0.5Cu	209–212	6,000–9,000
91.5Sn/3.5Ag/1.0Bi/4.0In	208–213	10,000–12,000
92.8Sn/0.7cu/0.5Ga/6.0In	210–215	10,000–12,000
95.4Sn/3.1Ag/1.5Cu	216–217	6,000–9,000
96.2Sn/2.5Ag/0.8Cu/0.5Sb	216–219	6,000–9,000
96.5Sn/3.5Ag	221	4,186
99.3Sn/0.7Cu	227	1,125
Reference 63Sn/37Pb	183	3,656

The alloy also has impressively higher strength than any of the binary alloys—63Sn/37Pb or 96.5Sn/3.5Ag or 99.3Sn/0.7Cu.

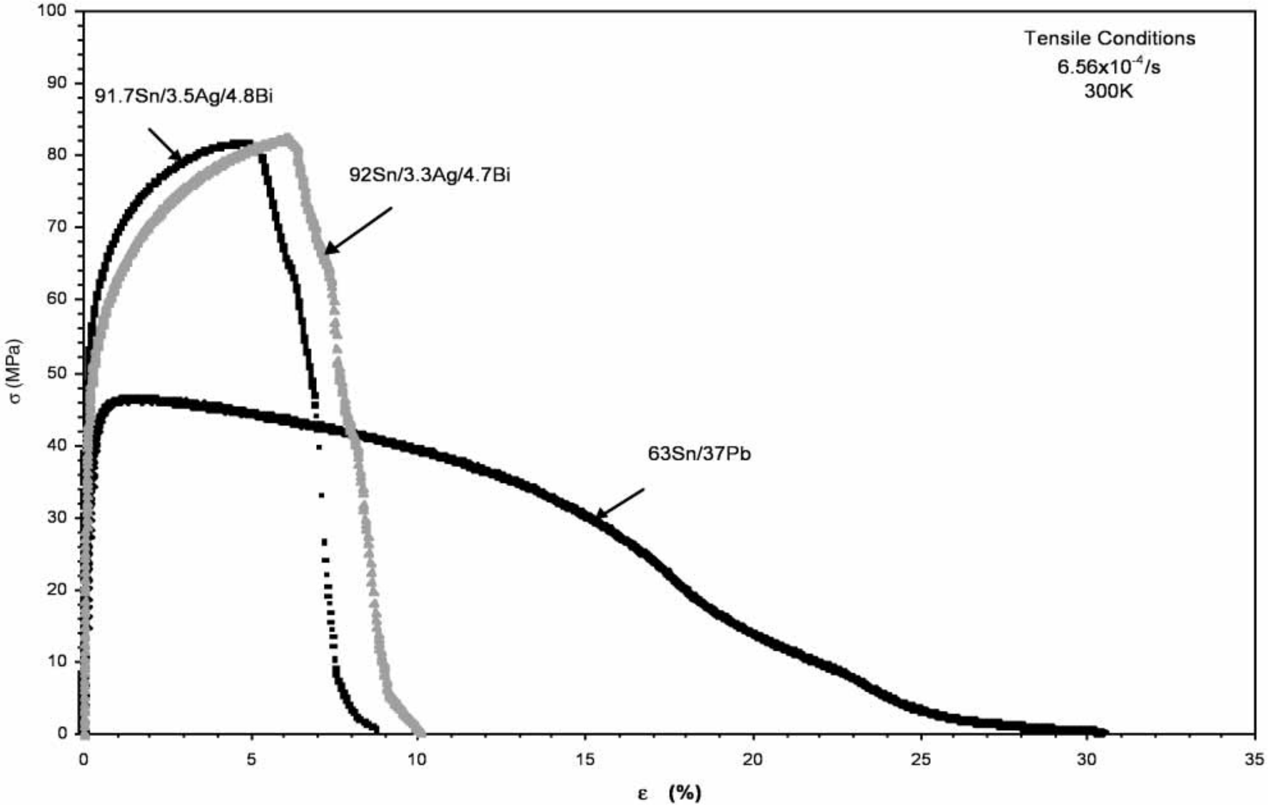


Figure 5.57 Tensile stress (σ) vs. strain (ε) at 300K and 6.56×10^{-4} /second for Sn/Ag/Bi alloys and 63Sn/37Pb.

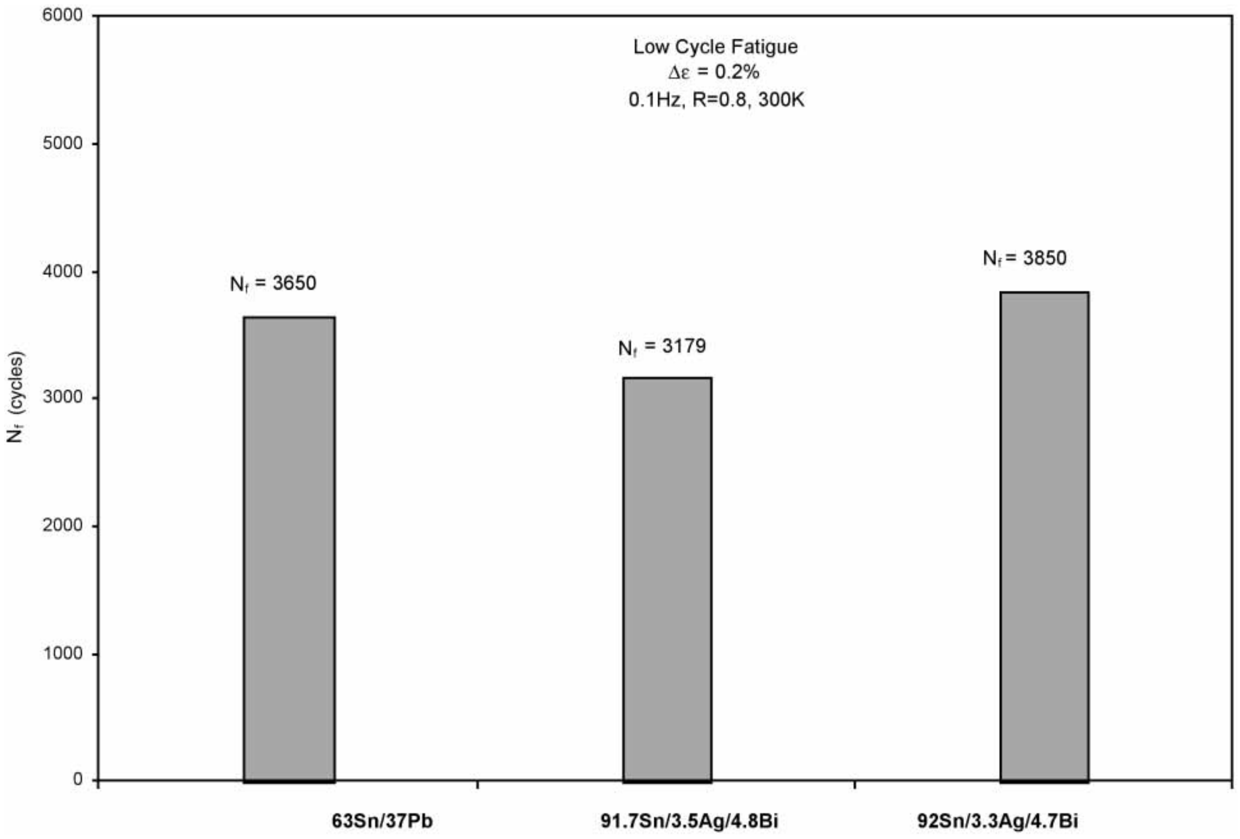


Figure 5.58 Comparison of fatigue life of Sn/Ag/Bi alloys with 63Sn/37Pb.

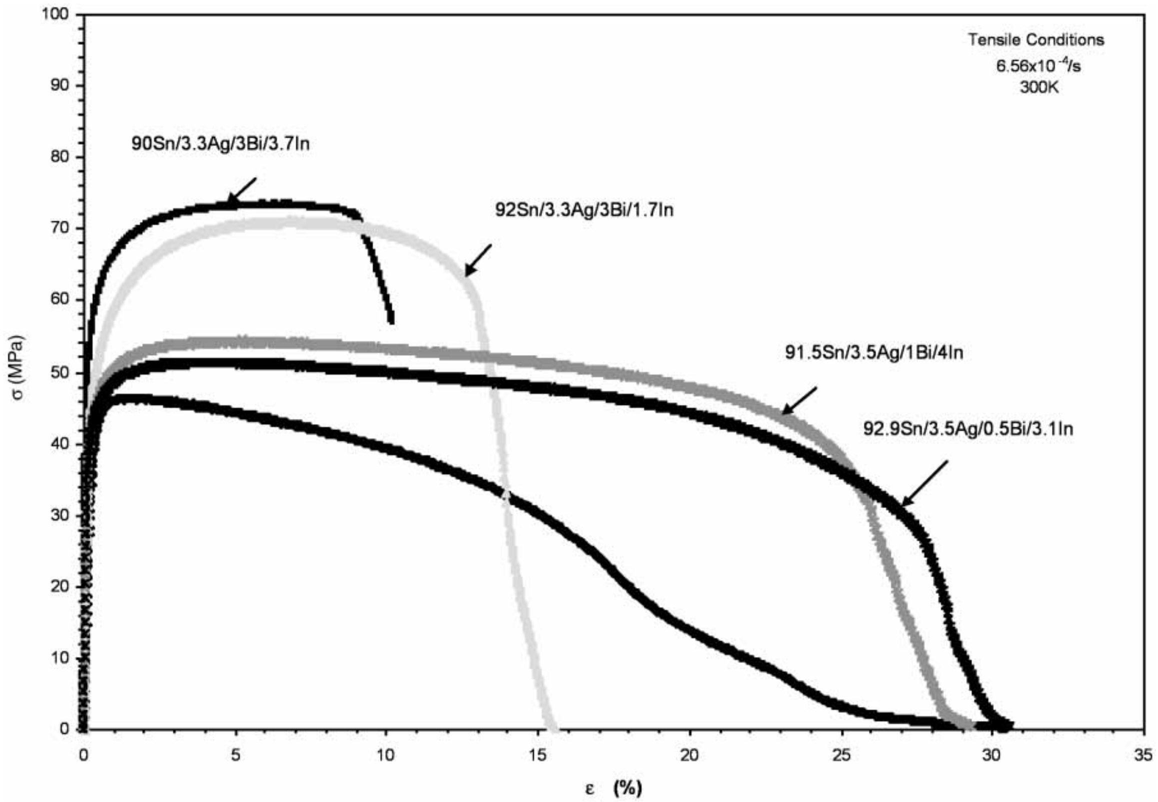


Figure 5.59 Tensile stress (σ) vs. strain (ε) at 300K and 6.56×10^{-4} /second for Sn/Ag/Bi/In alloys and 63Sn/37Pb.

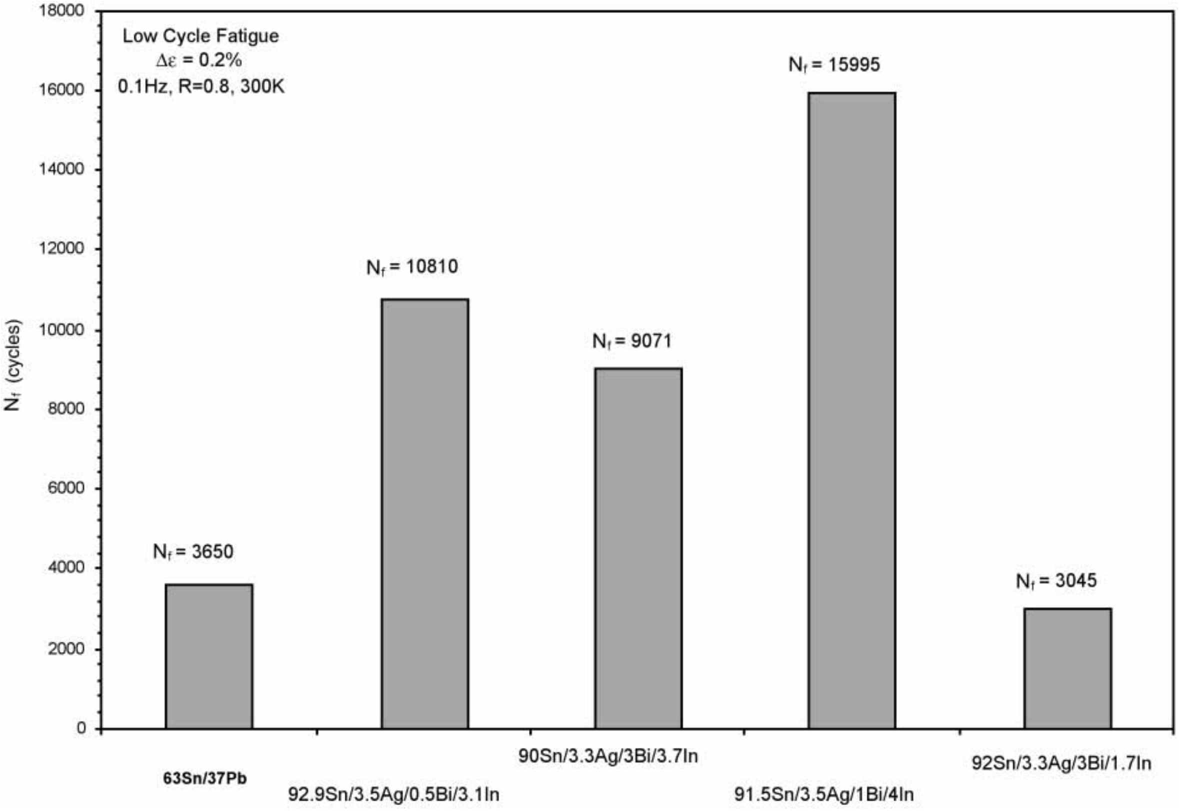


Figure 5.60 Comparison of fatigue life of Sn/Ag/Bi/In alloys with 63Sn/37Pb.

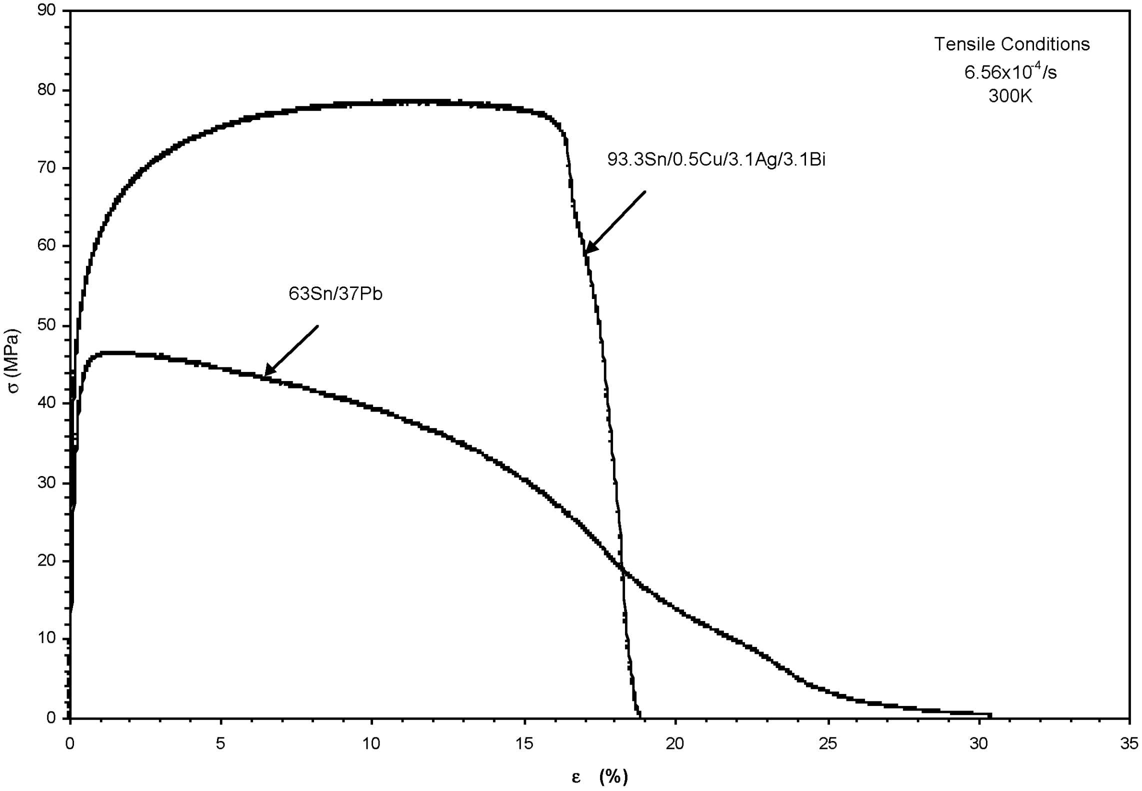


Figure 5.61 Tensile stress (σ) vs. strain (ε) at 300K and 6.56×10^{-4} /second for Sn/Ag/Cu/Bi alloys and 63Sn/37Pb.

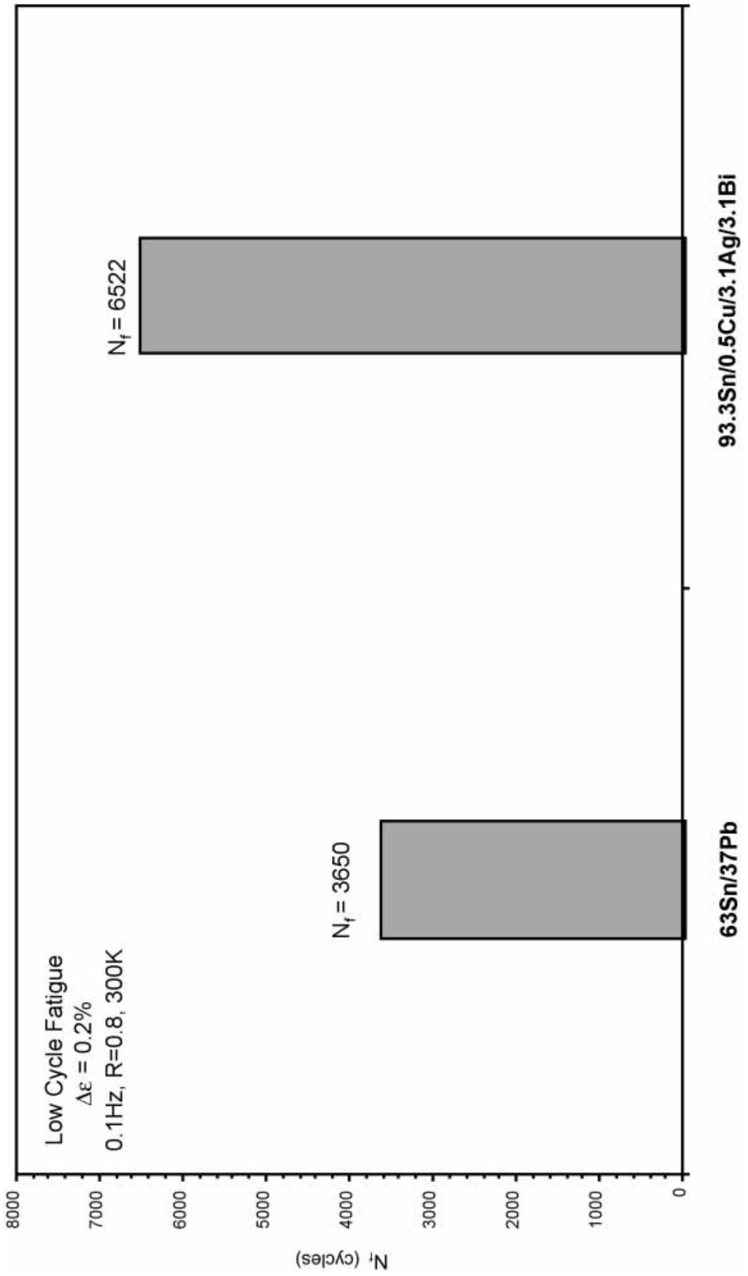


Figure 5.62 Comparison of fatigue life of Sn/Ag/Cu/Bi alloys with 63Sn/37Pb.

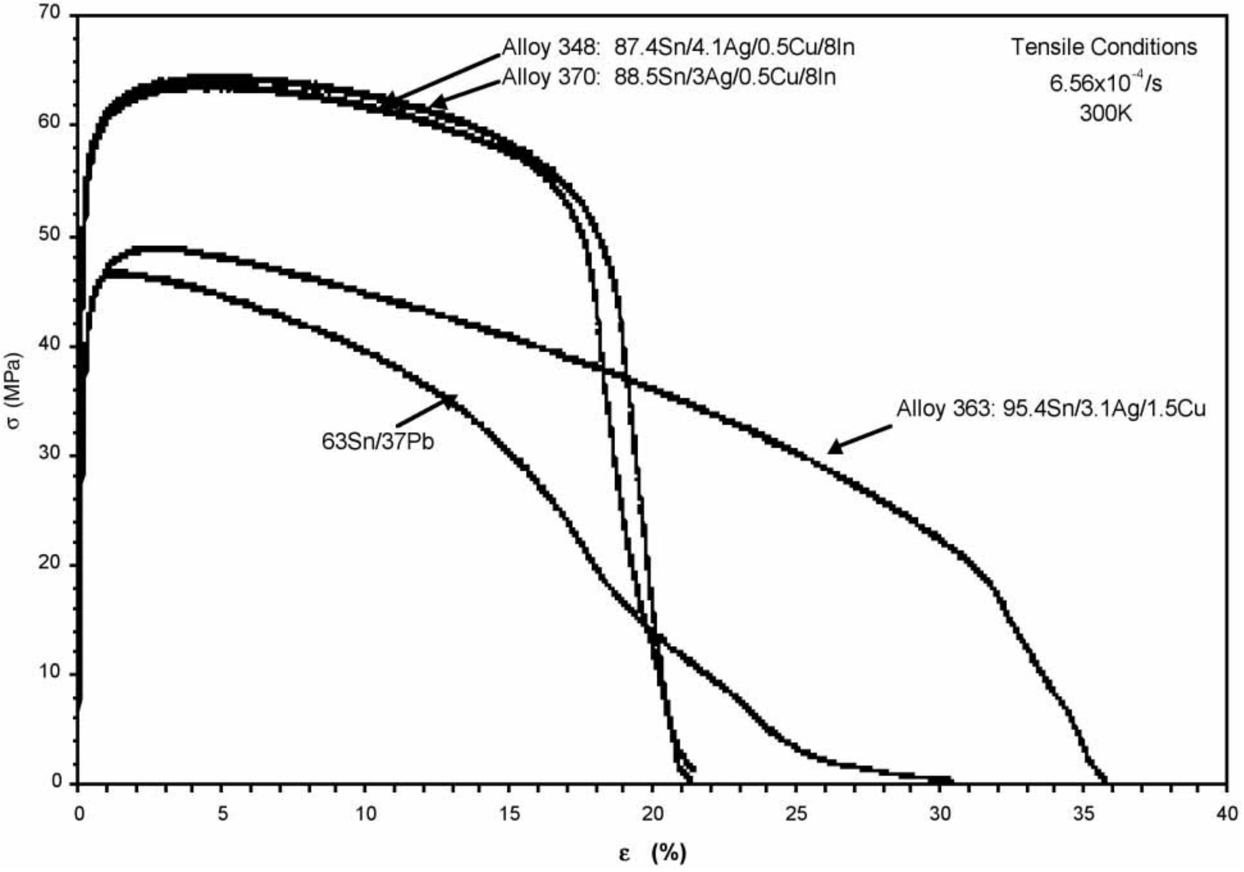


Figure 5.63 Tensile stress (σ) vs. strain (ε) at 300K and 6.56×10^{-4} /second for Sn/Ag/Cu/In alloys and 63Sn/37Pb.

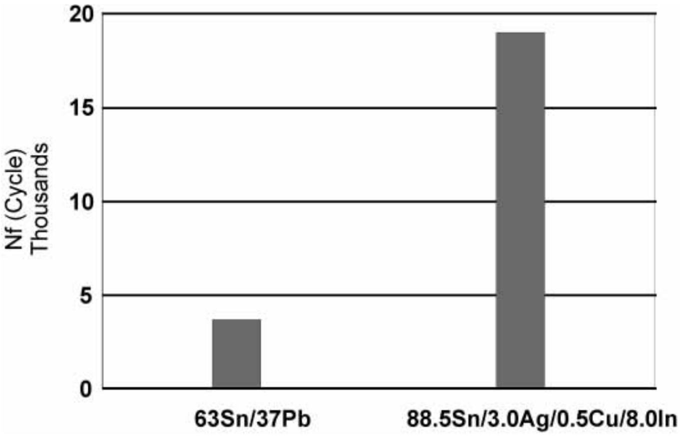


Figure 5.64 Comparison of fatigue life of Sn/Ag/Cu/In alloys with 63Sn/37Pb.

TABLE 5.17 Ranking of Viable Alloy Compositions by Fatigue Resistance

Alloy	Melting T°C	N_f
88.5Sn/3.0Ag/0.5Cu/8In	195–201	>19,000
91.5Sn/3.5Ag/1.0Bi/4.0In	208–213	10,000–12,000
92.8Sn/0.7Cu/0.5Ga/6.0In	210–215	10,000–12,000
85.2Sn/4.1Ag/2.2Bi/0.5Cu/8.0In	193–199	10,000–12,000
93.3Sn/3.1Ag/3.1/Bi/0.5Cu	209–212	6,000–9,000
96.2Sn/2.5Ag/0.8Cu/0.5Sb	216–217	6,000–9,000
95.4Sn/3.1Ag/1.5Cu	216–217	6,000–9,000
96.5Sn/3.5Ag	221	4,186
92Sn/3.3Ag/4.7Bi	210–215	3,850
99.3Sn/0.7Cu	227	1,125
Reference 63Sn/37Pb	183	3,650

5.11.6 Pb-free recommendations

- An optimal composition should be determined based on the required the performance level for a specific application. Tables 5.16 and 5.17 provide the relative performance of the selected alloys that show the most promise.
- A slate of compositions as listed below can be considered:

Sn/3.0-3.5Ag/0.5-0.5Cu/4.0-8.0In
Sn/3.0-3.5Ag/3.0-3.5Bi/0.5-0.7Cu
Sn/3.3-3.5Ag/1.0-3.0Bi/1.7-4.0In

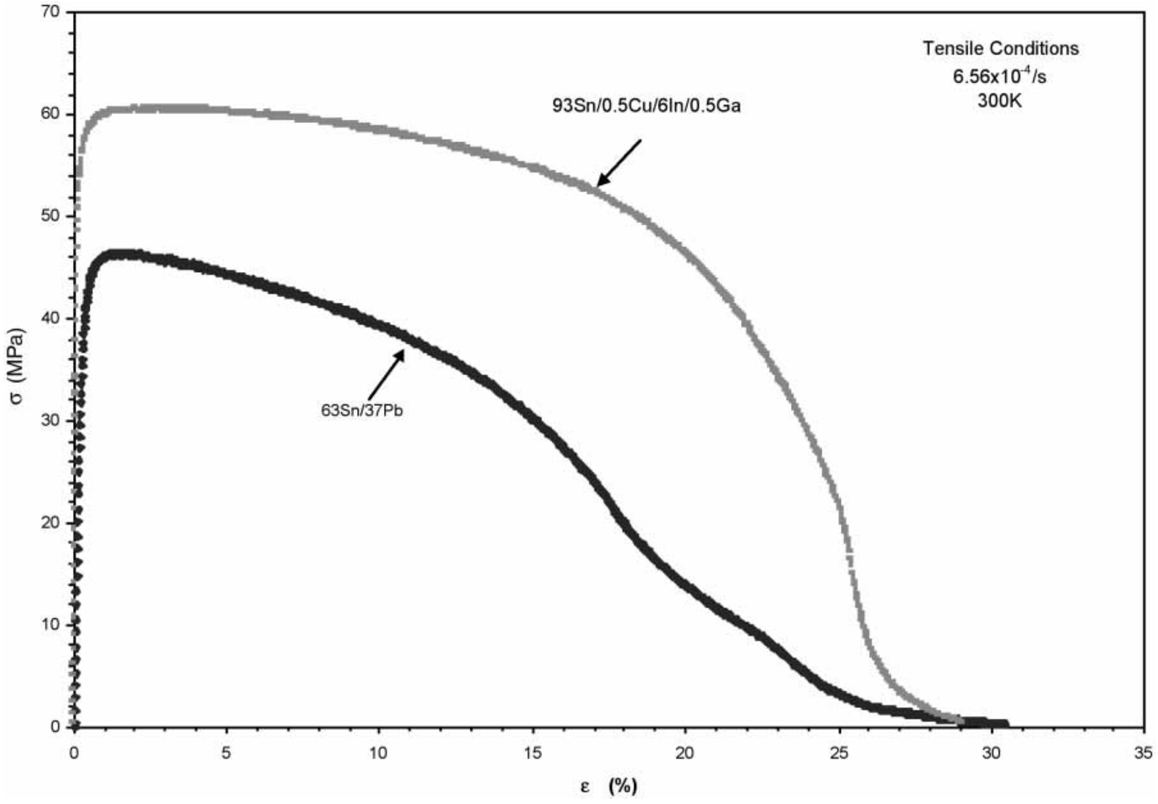


Figure 5.65 Tensile stress (σ) vs. strain (ε) at 300K and 6.56×10^{-4} /second for Sn/Cu/In/Ga alloys and 63Sn/37Pb.

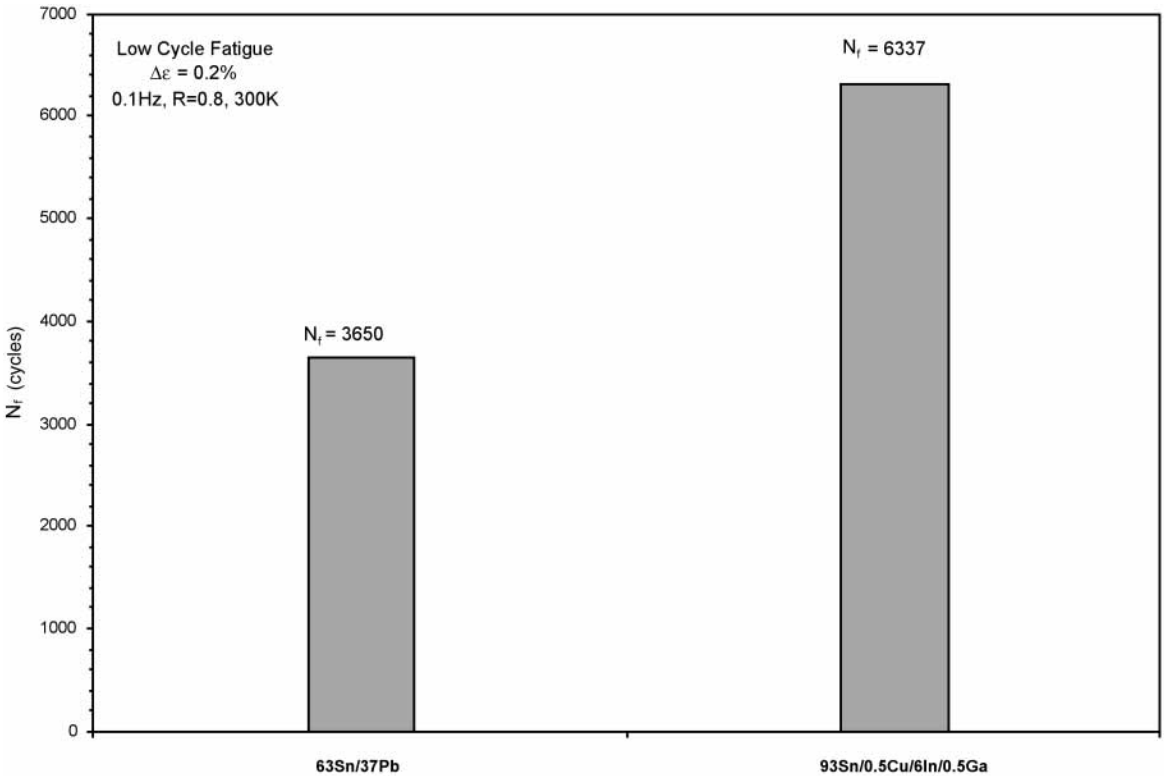


Figure 5.66 Comparison of fatigue life of Sn/Cu/In/Ga alloys with 63Sn/37Pb.

Sn/0.5-0.7Cu/5.0-6.0In/0.4-0.6Ga
Sn/3.0-3.5Ag/0.5-1.5Cu
Sn/3.0-3.5Ag/1.0-4.8Bi
99.3Sn/0.7Cu
96.5Sn/3.5Ag

- Melting temperature (liquidus temperature) is an important selection criterion.
- A proper reflow profile is able to compensate, to some extent, for the higher melting temperature (higher than 183°C) associated with lead-free alloys.
- For surface mount PCB assembly, the melting temperature of solder alloys below 215°C provides the necessary process window.
- For a reflow process, the peak temperature should be kept below 240°C, preferably 235°C; for wave soldering, the temperature should be below 245°C.
- Alloy intrinsic wetting ability is crucial to the quality and integrity of solder joints and the production yield.
- Overall, technological advancement has been made in enhancing creep and fatigue resistance by lead-free research and the viable alloys are identified for highly fatigue-resistant applications.

References

1. J.S. Hwang, *Solder Paste in Electronics Packaging*, Van Nostrand Reinhold, New York, 1989, ISBN 0442207549.
2. J.S. Hwang, *Advanced Solder Technology of Comparative Electronics Manufacturing*, McGraw-Hill, New York, 1996.
3. B. Champagne and R. Angers, "Size Distribution of Powders Atomized by the Rotating Electrode Process," *Mod. Devel. In Powder Metall.*, Vol. 12, pp. 83–104, 1980.
4. B. Champagne and R. Angers, "Fabrication of Powder by the Rotating Electrode Process," *Int. J. Powder Metall. Powder Technol.,* Vol. 16, No. 4, pp. 319–367, 1980.
5. B. Champagne and R. Angers, "Rotating Electrode Atomization Mechanisms," *Powder Metall. Int.,* Vol. 16, No. 4, pp. 125, 1984.
6. T. Takeda, Japan Nat. Research Inst. for Metals, Tokyo, Japan.
7. U. Backmark, N. Backstrom, and L. Arnberg, "Production of Metal Powder by Ultrasonic Gas Atomization," *Powder Metall. Int.,* Vol. 18, No. 5, 1986.
8. D.L. Erick, Battelle Memorial Inst., Columbus, OH.
9. J.S. Hwang, "New Developments in Fluxing and Fluxes," *Electron Packag. Prod.,* June 1990.
10. J.D. Ferry, *Viscoelastic Properties of Polymers,* Wiley, New York, 1979.
11. J.S. Hwang and N.C. Lee, "A New Development in Solder Paste with Unique Rheology for Surface Mounting," in *Proc. 1985 Int. Symp. on Microelectronics*.
12. E.F. Lish, Martin Marietta Corp., private communication.
13. E.A. Wright, "Laser versus Vapor Phase Soldering," *Soc. Advancement of Material and Processing Eng.,* 1985.
14. J.S. Hwang, "Controlled Atmosphere Soldering—Principles and Practice," in *Proc. NEPCON West,* pp. 1539–1546, 1990.
15. Norman R. Cox, "The influence of Varying Input Gas Flow on the Performance of a Nitrogen/Convection Oven," *Proceedings NEPCON East,* p. 323, 1994.
16. J.S. Hwang, "Soldering and Solder Paste Prospects," *Surface Mount Technol.,* Oct. 1989.
17. P. Ford and P.J. Lensch, "Cover Gas Soldering Leaves Nothing to Clean off PCB Assembly," *Electron. Packag. Prod.,* Apr. 1990.

18. E. Small, "No-Clean Fluxes: New Technology Needs New Test," *Circuits Manuf.,* Dec. 1989.
19. James B. Halbert, "Solvent cleaning of SMDs with Boiling and Quiescent Ultrasonics," Surface Mount Compendium, IEPS
20. J. S. Hwang, *Ball Grid Array and Fine Pitch Peripheral Interconnections,* Electrochemical Publications, Great Britain, 1995, ISBN 0901150290.
21. D.B. Barker, I. Sharif A. Dasqupta, and M.G. Pecht, "Effect of SMC Lead Dimensional Variabilities on a lead compliance and solder joint fatigue life," *Journal of Electronic Packaging,* Vol. 114, p. 117, June 1192.
22. J.S. Hwang, G. Lucey, R.B. Clough, and J. Marshall, "Futuristic Solders—Utopia or Ultimate Performance," *Surface Mount Technology,* September 1991, p. 40.
23. William B. Hampshire, "The Search for Lead-Free Solders," *Proceedings SMI Conference,* 1992, p. 729.
24. J.S. Hwang and Z. Guo, "Lead-Free Solders for Electronic Packaging and Assembly," *Proceedings SMI Conference,* 1993, p. 732.
25. J.S. Hwang, "Overview of Lead-Free Solders for Electronic Microelectronics," *Proceedings Surface Mount International,* 1994, p. 405.
26. J.S. Hwang, "Modern Solder Technology for Competitive Electronics Manufacturing," McGraw-Hill, New York 1996, Chapter 15, ISBN 0070317496.
27. J.S. Hwang and H. Koenigsmann, "New Developments of Lead-Free Solders," *Proceedings Surface Mount International,* 1997.
28. H-Technologies Group, Inc. Internal Reports, 1996, 1997, 1998, 1999.
29. J.S. Hwang, "Solder Materials," *Surface Mount Technology,* March, 2002, p. 56.
30. J.S. Hwang, "Environment-Friendly Electronics—Lead Free Technology," 2001, *Electrochemical Publications, Great Britain,* ISBN 0-90-115040-1
31. J.S. Hwang, *Modern Solder Technology for Competitive Electronics Manufacturing*, 1996, McGraw Hill, New York.
32. G.K. Lucey, "Composite Solders," U.S. Patent No. 5,520,752
33. J.S. Hwang, "High Strength Lead Free Solder Materials," U.S. Patent No. 5,985,211
34. J.S. Hwang, "Lead-Free Solders," U.S. Patent No. 6,176,947
35. C. Melton, "Low Temperature-Wetting Tin-based Solder Paste," U.S. Patent No. 5,229,070.
36. A.Lubrano, "Low Toxicity Corrosion Resistant Solder," U.S. Patent No. 4,778,733.
37. T.E. Wylam, "No-leaded Solders," U.S. Patent No. 5,102,748.
38. H.S. Chen, "Article Comprising Pb-Free Solder having Improved Mechanical Properties," U.S. Patent No. 5,538,686
39. P.E. Naton, "Lead- and Antimony-Free Solder Composition," U.S. Patent No. 4,879,096.
40. I.E. Anderson, "Pb-Free Sn-Ag-Cu Ternary Eutectic Solder," U.S. Patent No. 5,527,628.
41. K.F. Seelig, "Lead-Free and Bismuth-Free Tin Alloy Solder Composition," International Patent WO 94/25634
42. R.M. Henson, "Solder Composition," U.S. Patent No. 4,670,217.

5.12 Suggested Reading

R. Prasad, "Lead Free Solder," *Surface Mount Technology*, p. 26, 2000.

S. Bhattacharya and D. Baldwin, "Gallium ally breakthrough for via-filling application," *Advanced Packing,* p. 61, September 2000.

National Center for Manufacturing Sciences Lead-free Solder Project, *Surface Mount Technology*, p. 73, February 2000.

J. Chappell, "Agilent Sees Through Lead," *Electronic News*, p. 26, May 22, 2000.

D. Shangguan and A. Achari, "Evaluation of lead-free Eutectic Sn-Ag Solder for Automotive Electronics Packaging Applications," *Proceedings IEEE International Electronics Manufacturing Technology Symposium,* p. 25, 1994.

M. Kwoka and D. Foster, "Lead finish comparison of lead-free solders versus eutectic solder," *Proceedings, SMI,* p. 102, 1994.

D. Suraski, "A study of antimony in solder," private communication.

B. Fuller and R. Wilson, "Researchers trying to bump lead from solder," *Electronic Times,* p. 7, September 6, 1999.

I. Anderson, K. Kirkland and W. Willenberg, "Implementing Pb-free soldering," *Surface Mount Technology,* p. 78, November, 2000.

A. Forsten, et. al., "Development and validation of lead-free wave soldering process," *Soldering and Surface Mount Technology,* p. 29, 12/3, 2000.

T. Kim, "Impending technology requires industry support for advanced packaging," *Advanced Packaging,* November/December, p. 52, 1999.

J. Carlton, "Environmentalists to fight globalization," *The Wall Street Journal,* July 17, 2000.

R. Gleen and J. Smetana, "Some fundamental concerns in lead-free implementation," *Proceedings Lead Free Interconnect Technology Symposium, SMTA,* p. 7, June 2000.

A. Rae, "A strong vote for lead-free processing," *Proceedings Lead Free Interconnect Technology Symposium,* SMTA, p. 1, June 2000.

P. Biocca, "Lead-Free Alloys for Wave and SMT Assembly—with Two Alloys," *Proceedings Lead Free Interconnect Technology Symposium,* SMTA, June 2000, p. 42.

K. Lin, et. al., "The interaction of Sn-Ag and Sn-Ag-Cu solder balls with BGA pad," *Proceedings Lead Free Interconnect Technology Symposium,* SMTA, p. 47, June 2000.

L. Kloeser, "Lead free solders for area array packaging," *Proceedings Lead free Interconnect technology Symposium,* SMTA, p. 69, June 2000.

G. Diepstraten, "Analyzing lead-free wave soldering defects," *Surface Mount Technology,* p. 48, October 2000.

www.npl.co.uk/npl/ei/index.html

www.panasonicfa.com

J.S. Hwang, "Modern Solder Technology for Competitive Electronics Manufacturing," Chapter 5, McGraw-Hill, New York, New York, 1996.

Texas Instruments Report, Shelf-life evaluation of Ni/Pd lead finish for integrated circuits.

D. Romm and N. McLellan, Texas Instruments Report, Palladium lead finish.

Ken Snowdon, "Lead Free—the Nortel Experience," *Conference Proceedings, IPC Works '99*, October, 1999, p. S-05-1-4.

D. Romm and D. Abbott, Texas Instruments Report, Pb-Free Solder Joint Evaluation.

C. Fan, J. Abys, and A. Blair, "Nickel/palladium-plated leadframes," *Circuits Assembly,* p. 80, September, 1998.

D.C. Abbott, "Nickel/palladium finish for leadframes," *Conference Proceedings, IPC Works'99,* October, 1999, p. S-02-4-9.

B.F. Stacy, I.V. Kadija, L.J. Mayer, E.J. Kudrak, C. Fan, J.A. Abys, and H.K. Straschil, "Palladium for PWB Applications," *Conference Proceedings NEPCON-West,* 1997, p. 1569.

D.C. Abbot, R.A. Frechette, G. Haynes, and D.W. Romm, "Shelf-Life Evaluation for Palladium-Finish ICs," *Circuits Assembly,* p. 40, July 1998.

P. Seto, J. Evans, and S. Bishop, "Analysis of the Palladium Finish," *SMT,* p. 60, June 1999.

E.E. Benedetto, "Evaluation of Palladium Lead," *SMT,* p. 90, February, 1999.

C. Hunt, "An Assessment of Lead-Free Palladium-Finished Components: The Impact on Assembly Yields with Conventional Tin/lead Solder," *Conference Proceedings, IPCWorks '99,* 1999, p. S-02-2-1.

Nikkei Sangyo, Tokyo, Japan, November, 1998.

R. Schetty, "Pb-free Component Finishes," *Conference Proceedings, IPC Works'99,* 19999, p. S-02-3-1.

C. Fan, J. A. Abys, and A. Blair, "Wirebonding to Palladium Surface Finishes," *Conference Proceedings NEPCON-West,* p. 1505, 1999.

V. Sloberg, "The Impact of PC Board Surface Finish on SMT Assembly Process Yield and Reliability," *Chip Scale Review,* p. 65, July/August, 1999.

J. Guy, "Solder Joint Reliability Impact of Using Immersion Metallic Coatings," *Conference Proceedings NEPCON-West,* p. 1540, 1997.

J. Baliga, "Tin for No-Lead Solder," *Semiconductor International,* p. 74, July, 1999.

D.H. Ormerod, "The Development and Use of a Modified Immersion Tin as a High Performance Solderable Finish," *Conference Proceedings NEPCON-West,* p. 1515, 1999.

D.H. Ormerod, "Production Application For Flat Tin Finishes," *Conference Proceedings NEPCON-west,* p. 860, 2000.

D.P. Cullen, "New Generation Metallic Solderability Preservatives: Immersion Silver Performance Results," *Journal of SMT,* p. 17, October, 1999.

L. Lee Parker, "The Performance and Attributes of the Immersion Silver Solderability Finish," *Conference Proceedings NEPCON-West,* p. 444, 1999.

E. Stafsrom, K. Wengenroth, "OSPs: The Next Generation," *Conference Proceedings NEPCON-west,* p. 875, 2000.

T.J. Baggio, K. Suetsugu, and T. Okumura, "Challenges and Solutions for Lead-Free Soldering of Large PCB Assembly," *Conference Proceedings Apex, 2000,* p. P-MT3/1-4.

ANSI-STD-003.

K. Feldmann and M. Reichenberger, "Assessment of Lead-Free Solders for SMT," *Conference Proceedings APEX, 2000*, p. P-MT2/2-3.

G.L. Bailey and H.C. Watkins, "The Flow of Liquid Metals on Solid Metal Surfaces and its Relation to Soldering, Brazing and Hot-Dip Coating," *I. Ins. Metals,* Vol. 80, p. 57, 1951–1952.

G. Ghosh and M.E. Fine, "Tin Base Solder Contains Silver and Indium," International Patent WO 97/43456.

J.H. Vincent and G. Humpston, "Lead-Free Solders for Electronic Assembly," *GEC Journal of Research,* Vol. 11. No. 2, pp. 76–89, 1994.

P. T. Vianco, I. Artaki, and A. M. Jones, "Assembly Feasibility and Reliability Studies of Surface Mount Boards Manufactured with Lead-Free Solders," SMI'94.

D. Shangguan and A. Achari, "Evaluation of Lead-free Eutectic Sn-Ag Solder for Automotive Electronics Packaging Applications," *Proc. 1994 IEEE/CPMT Intl. Electronic Manufacturing Technology Symposium,* pp. 25-37.

N.F. Mott and F.R.N. Nabarro, "Report on Conference on the Strength of Solids," *Phys. Soc.,* London, p. 1, 1948.

F. Hua and J. Glazer, "Lead-Free Solders for Electronic Assembly," *TMS Design and Reliability of Solders And Solder Interconnections,"* pp. 66–73.

F.M. Hosking, P.T. Vianco, C.L. Hernandez, and J.A. Rejent, "Wetting Behavior of Alternative Solder Alloys," *SMI'93*, pp. 476–483.

C.E. Tallis, "Solder," UK Patent GB 2158459, November 13, 1985.

K.G. Snowdon, C. G. Tanner, D. P. Francis, G. Mackerness and T. Bowden, "Applications of Lead Free Solders in the Telecommunications Industry," *Future Circuits International,* pp.21–25.

R.E. Pratt and B. Trumble, "Process and Material Characterization for Lead-Free Tin-Copper Solder Alloy," pp. 589–602.

R. Labusch, "A Statistic Theory of Solid Solution Hardening," *Phydica Status Solidi*, Vol. 41, pp. 659–669,1970.

J.H. Vincent, B.P. Richards, D.R. Wallis, I.A. Gunter, M. Warwick, H.A.H. Steen, P.G. Harris, M.A. Whitmore, S.R. Billington, A.C. Harman, and E. Knight, "Alternative Solders for Electronics Assemblies," *Circuit World*, Vol. 19, No. 31, pp. 32–34, 1993.

C. Madore, D. Landolt, C. Habenpflug, and J.A. Hermann, "Application of the Rotating Cylinder Hull Cell to the Measurement of Throwing Power and the Monitoring of Copper Plating Baths," *Plat. and Surf. Fin.*, 82, 36 1995.