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Chapter 2. Materials for Building Electrical Connections

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Abstract—In this chapter, we comprehensively discuss the primary varieties of solders and fluxes utilized in the fabrication of electrical connections within electronic modules. Particular emphasis is placed on the challenges associated with the use of lead-free soldering materials. A potential resolution to these challenges involves the modification of solder compositions, potentially transitioning towards nanoscale architectures. A promising avenue of exploration lies in the utilization of water-based fluxes and flux gels. Water-based fluxes containing surfactant additives offer notable advantages, particularly in their application via spray mechanisms. They exhibit robust stability and mitigate thermal shock occurrences during soldering operations. Furthermore, we delve into the characteristics of solder pastes employed in the surface mounting of electronic modules, elucidating their application methodologies, operational considerations, and optimal storage practices. Additionally, we provide a comprehensive overview of conductive adhesives utilized in the formation of contact connections. The chapter also examines the primary types of mounting microwires employed in ultrasonic and thermosonic microwelding processes, alongside outlining the role of protective liquids in the cleaning of connections.

Keywords: solders, fluxes, pastes, conductive adhesives, microwires

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1. SOLDER ALLOYS FOR ELECTRICAL CONNECTIONS

Solders intended for hot tinning of surfaces and forming soldered joints of electronic components during assembly and construction of electronic devices must meet the following requirements: high mechanical strength under specified operating conditions, high electrical and thermal conductivity, sealing properties, corrosion resistance, liquidity at soldering temperature, good wetting of the base metal, and a small crystallization temperature range. According to their melting points, solders are classified into the following groups (GOST 19248-90): extra-low melting ($T_m \leq 145°C$), low melting ($145°C < T_m \leq 450°C$), medium melting ($450°C < T_m \leq 1100°C$), and high melting ($T_m > 1100°C$). The previous classification (soft low-temperature solders with $T_m < 450°C$ and hard high-temperature solders) is obsolete. In electronics, solders of the first three groups are used predominantly. The main group of low-melting solders belong to the tin–lead (Sn–Pb) system (Fig. 1).

The eutectic alloy (61% Sn, 39% Pb) possesses the lowest melting temperature (183°C). At concentrations of Sn in the melt from 0 to 20%, a tin-rich α-solid solution forms, while at 97.5%, a lead-rich β-solid solution forms. Above the liquidus line in the tin concentration range from 20 to 60%, an α-solution forms, meaning the melt contains undissolved lead particles, while at tin concentrations from 60 to 97.5%, a β-solution forms. The composition, melting temperatures, and application areas of Sn–Pb solders are listed in Table 1. Drawbacks of Sn–Pb solders include their embrittlement and creep at temperatures above 100–150°C. Solders such as 30SnPb and 40SnPb have wide crystallization temperature intervals, which affect soldering process efficiency. By introducing alloying additives into the Sn–Pb system, solders with

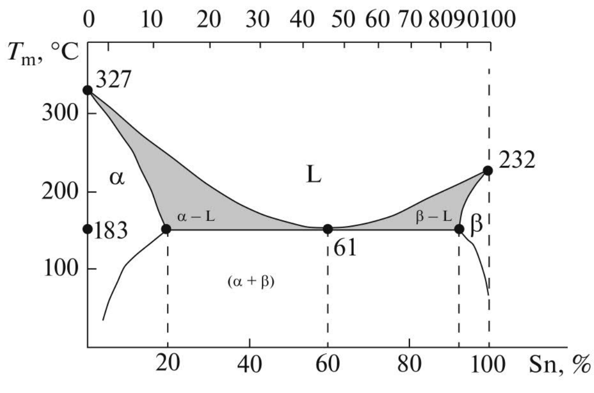

Fig. 1. Phase diagram of the Sn–Pb system.

Table 1. Properties tin–lead solders

Solder grade	Compound, %, Lead is the rest	Melting point, °C	Application area
POS 30	Tin 29–30, antimony 1.5–2.0	183–256	Structural soldering of copper, its alloys, and carbon steels
POS 40	Tin 39–40, antimony 1.5–2.0.	183–235	Soldering and tinning of parts made of copper alloys and steels
POS 61	Tin 59–61, antimony up to 0.8	183	Assembly soldering, tinning of component and IC leads
POS 61M	Tin 59–61, antimony up to 0.8, copper 1.5–2.0.	183–185	Soldering wiring connections with a soldering iron
POS 63	Tin 63 ± 0.5, impurities 0.15	183–185	Wave soldering of multilayer printed circuit boards
POS 90	Tin 90	183–222	Soldering parts on silver and gold coatings

Table 2. Properties of special solders

Solder grade	Compound, % Lead is the rest	Melting point, °C	Application area
POSSu 102	Tin 8–10, antimony 2–3	268–285	Soldering joints with increased strength
POSK 5018	Tin 50, cadmium 18	142–145	Soldering elements sensitive to overheating
POSV 33	Tin 33, bismuth 33	120–130	Tinning of printed circuit boards
POSV 50 (Rose's alloy)	Tin 25, bismuth 50	90–92	Tinning of PCB and multilayer PCB
POSV 50K (Wood's alloy)	Tin 12.5, cadmium 12.5, bismuth 50	66–70	Soldering fuses
POI_N 50	Tin 50, indium 50	117	Soldering of hybrid ICs, large-scale hybrid ICs, ferrite, and ceramic substrates
PSr 45	Silver 45, copper 30, zinc 25	660–725	Soldering of copper and steel products under increased static and vibration loads
PSr 2.5	Tin 5, silver 2.5	295–305	Soldering of waveguides with silver coating
PSr 1.5	Tin 15, silver 1.5	265–270	Soldering of connections operating at temperatures up to 200°C
POSSr 2	Tin 60, silver 2	169–173	Soldering and tinning on silver coatings
P150A	Tin 40, zinc 3.5	150–165	Soldering and tinning of ceramics and ferrites with ultrasound
POTs 10 (P200A)	Tin 90, zinc 10	199–210	Soldering and tinning of ceramics with ultrasound
POTs 20 (P250A)	Tin 80, zinc 20	200–250	Soldering aluminum and titanium alloys with ultrasound
P300A	Cadmium 40, zinc 60	266–310	Soldering aluminum and titanium alloys with ultrasound
POS 313	Tin 60, gold 3.0	180–215	Soldering of semiconductor devices
PGlM 65	Gallium 65, copper 34–36	50	Soldering of heat-sensitive elements with self-strengthening connections

enhanced mechanical strength (Sb), lowered melting temperature (Bi, Cd, In), increased electrical conductivity (Ag), suitability for ultrasonic soldering and metallization (Zn), and soldering of semiconductor devices (In, Au, Ga) can be obtained (Table 2).

The selection of solder alloy is determined by the required mechanical strength and electrical conductivity of the joints, the maximum allowable soldering temperature, the type of base metal and surface finish, as well as techno-economic and technological requirements. The most common solder alloy for assembly soldering is the tin–lead solder 61SnPb, which is characterized by low melting temperature, a narrow crystallization interval, good fluidity, and low electrical resistance.

These factors contribute to the application of batch soldering methods with high productivity.

The copper-enriched solder 61SnPbCu is mainly intended for manual soldering, as it slows down the erosion of the soldering tip. For the assembly of plug, high-frequency, and coaxial connectors, cables requiring high heat, low-lead 40SnPb and 30SnPb solders are used. Soldering and tinning of thermosensitive elements are performed with low-melting solders 50SnPb18Cd, 50SnPb50Bi, and 33SnPb33Bi. Soldering of parts with coatings containing silver, gold, indium, or palladium is carried out using solders containing these elements.

Lead-based solders (e.g., 61SnPb) have gained wide acceptance in soldering technology due to their good wetting of certain metals (copper, nickel, gold, silver) and low soldering temperature (190–250°C).

2. PROPERTIES OF SOLDER ALLOYS DEPENDING ON COMPOSITION AND IMPURITY CONTENT

A significant drawback of lead-based solders is their active physicochemical interaction, both in the molten state and in the solid phase, with a range of metals (Au, Ag, Pd, Pt, Cu, Ni), used either in compact form (plates, wires) or as thin coatings 1–10 μm in thickness. The products of interaction between solders and these metals, namely intermetallic compounds (especially in the form of a continuous layer thicker than 3–5 μm), can significantly affect the strength of the interconnections [1].

Metallic wires show low dissolution rates in the molten solder of the Sn–Pb system, namely 0.043, 1.56, 0.021, and 0.356 μm/s for Ni, Pt, Pd, and Cu at 371°C, respectively. The dissolution rate of copper remains at 1.56 μm/s. Solders with low tin concentrations dissolve copper to a lesser extent (0.0457 μm/s). Adding copper (0.75–2.3%) to the eutectic Pb–Sn solder also decreases the dissolution rate of copper. Therefore, for soldering copper coatings, it is recommended to use solders with low tin concentration as well as eutectic solder modified with copper. However, when the liquid solder moves rapidly relative to the material being soldered, the dissolution rate may exceed the aforementioned rates several times. When soldering connections with a 61SnPb solder, coatings of Ni, Pt, Pd, or their alloys (Ni–Pd, Ni–Pt) can be used as barrier layers [2].

In a two-layer Au–Sn contact system obtained by molecular beam condensation in a vacuum, mutual diffusion in the solid phase of the system components is observed at room temperature. Over 48 h, the two-layer film system (with film thicknesses of 1.7 and 3.0 μm for Au and Sn films, respectively) transformed at 20°C into a film of uniform composition corresponding to the AuSn phase. This fact indicates the chemical incompatibility of gold with tin in nondismountable connections.

Another drawback of tin-based and indium-based solders is that the thermal expansion of tin and indium, which have a tetragonal crystal structure, is extremely anisotropic: the coefficient of linear expansion along the main crystal axis is approximately twice as large as the coefficient of linear expansion in the direction perpendicular to the main axis. Mechanical stress resulting from the anisotropy of the coefficients of linear expansion of tin grains and temperature changes is quite significant. During the thermal cycling of solders such as 61SnPb and 61SnPbCu, which contain 1–4% of copper, with heating to 160°C and cooling to 20°C over 30 s after 4000–5000 cycles, the tensile strength of the 61SnPb solder decreases by 2.5–3.0 times [3]. Fatigue phenomena in the solder develop faster in the presence of copper, and resistance to thermal cycling decreases with increasing copper concentration.

Table 3. Maximum impurity concentrations in Sn–Pb solders

Impurity	Maximum concentration, %
Antimony	0.5
Copper	0.3
Bismuth	0.25
Gold	0.2
Silver	0.1
Arsenic	0.03
Iron	0.02
Nickel	0.01
Aluminum	0.006
Zinc	0.005
Cadmium	0.005
Total Cu, Au, Cd, Zn and Al	0.4

Impurities in solder melts can originate from the materials of electronic component leads and printed circuit boards, erosion of the bath or crucible, and mixing of solders of different compositions. The maximum allowable impurity levels are specified in the IPC jSTD006 standard (Table 3).

During thermal cycling, the formation of fatigue cracks typically begins at the periphery of the solder joint, near the interface between the solder and the substrate of the integrated circuit (IC) and the wire lead. Fatigue damage occurred at phase boundaries rich in tin and lead, with cracks primarily propagating along these boundaries. The eutectic Sn–Pb alloy exhibits a greater propensity for initiating fatigue microcracks. Significant plastic deformation of the solder joint occurred in the high-temperature part of the thermal cycle (100–140°C), while at low temperatures (–50°C), the solder joints are stronger and thus can withstand stress approximately twice as much.

To enhance the fatigue strength, the grain boundaries of tin-based solders are reinforced with dispersed particles of intermetallic compounds like Ni_3Sn, and the solders are also reinforced with nickel, iron, and cobalt, with the particle size of 40–100 μm added at 5–15 wt % [4]. The effectiveness of the strengthening action of the second-phase particles, stable with the

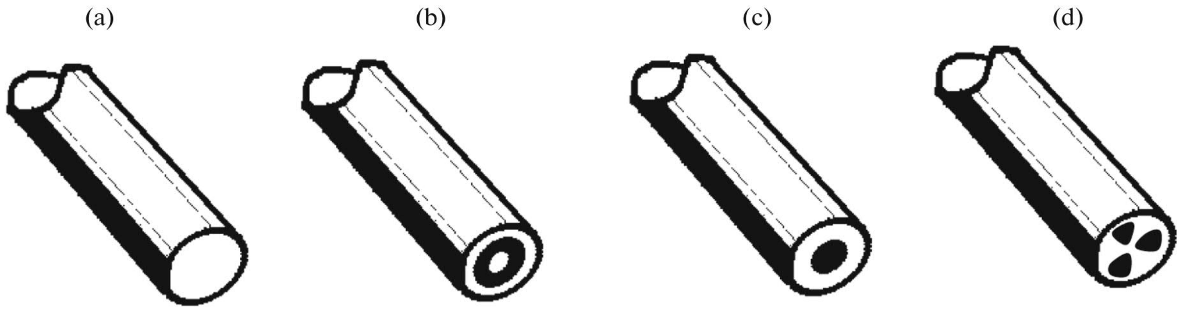

Fig. 2. Structure of tubular solders.

metallic matrix, is determined by the geometric parameters of the structure. The maximum effect is achieved under the following conditions: the size of reinforcing particles should not exceed 0.01–0.05 μm; the average distance between reinforcing particles should be 0.1–0.5 μm with their uniform distribution in the matrix; the quantity of reinforcing phase should not exceed 5–10%. Therefore, large particles of nickel and iron, forming solid solutions and chemical compounds with tin, cannot serve as a strengthening phase for tin and tin-based solders. Effective strengtheners can be highly dispersed particles of titanium dioxide or tungsten, which are chemically stable in contact with the tin matrix of dispersion-strengthened solder.

During the operation of devices with soldered joints based on tin, there is a risk of failure of components such as ferrite, ceramic substrates of integrated circuits (ICs), silicon, and germanium crystals of semiconductor devices, especially under severe thermal conditions, particularly at low ambient temperatures. The loss of ductility of tin-based solders at low temperatures affects the resistance of soldered joints to thermal shocks.

Solders based on tin–indium alloys are used for soldering thermally sensitive devices, the maximum allowable temperature of which does not exceed 150–250°C. The drawbacks of solders with high indium concentration include low melting temperature (120–156°C), low strength of indium, anisotropy of thermal expansion, and increased chemical reactivity towards most metals.

Solders are produced in the form of solid (Fig. 2a) or pressed (Fig. 2b) wire, where solder grains are surrounded by rosin, with a total concentration of 0.8–2.2 wt %. They are also available in flux-filled single (Fig. 2c), three-channel (Fig. 2d), or five-channel tubes. The use of tubular solder during manual soldering decreases solder consumption by 30–40% due to optimal dosing. Tubular solders from the Crystal series by Multicore Solders, based on Sn60 and Sn62 alloys and containing up to 3% flux, leave minimal residues on the board and do not require cleaning.

3. LEAD-FREE SOLDER ALLOYS

The replacement of conventional solders with lead-free materials is not only a sign of the times but also a requirement set forth by international environmental commissions. The Restriction of Use of Certain Hazardous Substances (RoHS) directive of the European Union on environmental safety, effective from July 1, 2006, restricted the use of lead in new electrical and electronic equipment to no more than 0.01%.

The melting temperature of solders is the most essential among their thermal, mechanical, fatigue, and other properties. Table 4 presents some widely known types of lead-free solders [5]. Lead-free solders with high indium concentration are characterized by the incompatibility of indium and tin materials, regardless of whether the latter is present on the surface of the printed circuit board or the component leads. To implement fully a lead-free process, it may be necessary to utilize lead-free coatings on the soldered surfaces of the printed circuit board and component leads. Lead-free solders are characterized by either too low or too high melting temperatures compared to eutectic tin–lead solders. When using low-temperature solders, a special flux is required because alcohol-based fluxes are less active at low temperatures. Another limitation associated with low-temperature solders is the weakening of their wetting properties due to increased fluidity at subeutectic temperatures.

For low-temperature applications, solders containing indium have gained certain recognition. For example, many companies use a solder containing 52% In and 48% Sn because it ensures better characteristics for rework or repair processes. With a melting temperature of 118°C, this solder allows for multiple reflows at lower temperatures without the risk of thermal damage. If the boards are plated with gold as an anti-oxidant, using indium-containing solder prevents gold leaching. Another lead-free solder with a melting temperature of 138°C is the 42Sn–58Bi alloy; however, bismuth-containing alloys typically have poor wetting characteristics.