

## Chapter 4. Physicochemical Foundations of Electric Mounting Soldering

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**Abstract**—To ensure the formation of high-quality solder joints, it is imperative to engage in surface preparation of the materials being joined, activate both the materials and solder, eliminate oxide films in the contact zone, facilitate interaction at the interfacial boundary, and induce crystallization of the liquid metal layer. This chapter delves into the processes involved in removing surface oxide films from solderable surfaces and discusses the pertinent equipment employed. Additionally, it highlights the potential efficacy of ultrasonic methods in oxide film removal through the introduction of elastic mechanical vibrations into the molten solder. Mathematical expressions are derived to elucidate the dynamics at the solder-surface interface, during the capillary penetration of solder into gaps and the diffusion process. The formation of a soldered joint with a specific structure results from the physicochemical interaction between the solder and the base metal. This joint typically encompasses a melting zone and diffusion zone at the solder and the base metal interface. The ultimate structure and composition of the solder joint depend on the nature of the interacting metals, their chemical affinity, and the soldering conditions, including time and temperature.

**Keywords:** soldering, preparation for soldering, oxide films, ultrasonic cleaning, wetting, diffusion, soldered joint, structure

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### 1. SURFACE PREPARATION FOR SOLDERING

**Soldering** is a process of joining materials in the solid state by introducing a low-melting metal—solder—into the gap, which interacts with the base materials and forms a liquid metallic layer, the crystallization of which yields the solder joint. The definition implies that soldering occurs at temperatures significantly lower than the melting temperatures of the materials being joined, which lowers their overheating. Both metallic and nonmetallic materials can be joined, and an intermediate layer consisting of solder and its interaction products with the materials being soldered must form in the contact zone.

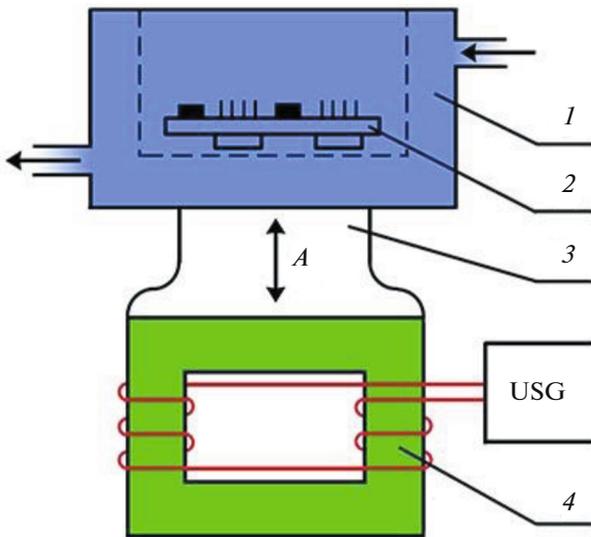
To form a quality solder joint, it is necessary to prepare the surfaces of the materials to be joined, activate the materials and solder, remove oxide films in the contact zone, ensure interaction at the interface between the materials, and create conditions for the crystallization of the liquid metallic layer.

Surface preparation for soldering involves mechanical, chemical, or electrochemical cleaning to remove oxides, organic, and mineral contaminants, as well as the application of coatings that improve soldering conditions or enhance the strength and corrosion resistance of soldered joints.

Mechanical removal of corrosion products and oxide films is carried out using cutting tools (files, grinding wheels, and scrapers), sandpaper, and wire mesh. To increase productivity when processing large or intricately profiled items, hydroabrasive cleaning is used, involving the use of a liquid jet or rotating brushes made of synthetic material with the addition of abrasive particles to the cleaning solution. The formation of a rough surface after mechanical processing promotes solder wetting, as the scratches on the surface act as tiny capillaries.

Removal of surface films that hinder wetting by molten solder can be accomplished using both chemical and electrochemical methods. Chemical degreasing of parts is carried out in a 5% solution of alkali or organic solvents such as acetone, benzene, alcohol, carbon tetrachloride, and alcohol–benzene, mixtures by wiping, immersion, spraying, vapor-phase treatment, or ultrasonic bath processing.

Ultrasonic degreasing is performed in special baths of both flowing and nonflowing types, where the bottom and walls undergo mechanical vibrations at ultrasonic frequencies (Fig. 1). For ultrasonic degreasing, UZV-0.1, UZV-0.25, and UZV-0.4 baths are used, operating at frequencies of 18–22 kHz in the precavi-



**Fig. 1.** Schematic diagram of ultrasonic cleaning in a flowing solution: (1) bath, (2) module, (3) concentrator, and (4) magnetostriuctive transducer; USG, ultrasonic generator.

tation mode, which ensures the generation of intense microflows in the cleaning liquid, guaranteeing high cleaning quality and speeding up the process by 5–10 times. The effectiveness of cleaning depends on the frequency and power of ultrasonic vibrations, processing temperature and time, as well as the composition of the solution and the degree of contamination.

Increasing the frequency enhances the penetrating ability of the solution by decreasing the wavelength of the ultrasonic vibrations and lowering the probability of damage to electronic components. Raising the temperature to 50–60°C increases the solubility of contaminants and enhances cavitation.

Thick layers of oxide films are removed by etching in acidic or alkaline solutions. The composition of the solution is determined by the type of metal, the thickness of the oxide film, and the required etching rate. Electrochemical etching accelerates the process of dissolving oxide films; it is carried out at a current density of 2–5 A/dm<sup>2</sup>. After etching, the parts are thoroughly rinsed in neutralizing solutions.

Cleaned parts should be immediately directed to assembly and soldering, as the solderability of copper lasts 3–5 days, and for silver, it lasts 10–15 days. Therefore, to ensure interoperation storage of parts and components, metallic coatings are applied to their surfaces, which improves the solder wetting process and maintains solderability for an extended period. Such coatings include low-melting solders (e.g., 61SnPb, SnPbBi), tin–bismuth or tin–nickel alloys, gold, silver, palladium, and other metals, which are applied by immersion in a melt, electroplating, thermal evaporation, or plating. In the former method,

immersion is carried out in solder melts after prefluxing. Galvanic coatings with noble metals are applied with a thickness of 3–6 μm, while the thickness of coatings with other metals can reach 6–9 μm. Films obtained by thermal vacuum deposition are characterized by high uniformity and absence of coating oxidation, but they have a small thickness (0.1–1.0 μm). Plating is performed by simultaneous rolling of the solderable metal and the coating metal, ensuring uniform coating thickness (100–150 μm). After completing preparatory operations or interoperation storage, the solderability of the parts is checked.

The activation of solderable surfaces is necessary for the physicochemical interaction of atoms of the base metal and solder. In this process, oxide films must be removed from the surfaces of the interacting metals, and the atoms must reach the required level of activation energy. At soldering temperature, when all atoms are excited, the reaction rate is [1]

$$\frac{dN}{dT} = (N_{\text{bm}} - N) \gamma e^{-Q/(kT_{\text{soldering}})}, \quad (1)$$

where  $N_{\text{bm}}$  is the number of contacting atoms on the surface of the base metal,  $N$  is the number of atoms that have entered into a chemical bond;  $\gamma$  is the frequency of natural vibrations of atoms (for metals  $1 \times 10^{13} \text{ s}^{-1}$ ),  $Q$  is the activation energy for the formation of a chemical bond,  $k$  is the Boltzmann constant ( $1.381 \times 10^{-23} \text{ J/K}$ ), and  $T_{\text{soldering}}$  is the soldering temperature, K.

By integrating the last equation with  $T_{\text{soldering}} = \text{const}$ , and the following initial and final conditions:  $t = 0, N = 0, t = t_{\text{soldering}}, N = N_{\text{soldering}}$ , we obtain the soldering time during which  $N_{\text{soldering}}$  metal atoms react,

$$t_{\text{soldering}} = -\frac{1}{\gamma} \ln \left( 1 - \frac{N_{\text{soldering}}}{N_{\text{bm}}} \right) e^{-Q/(kT_{\text{soldering}})}. \quad (2)$$

Therefore, the activation energy  $Q$  significantly affects the rate of interaction between the atoms of the base metal and the solder.

In their normal state, metal surfaces are covered with oxide films. Heating the base metal and the molten solder results in a decrease in their activity because of the interaction with oxygen in the air and the growth of oxide films on the surface. Removing oxide films during soldering is a necessary condition for obtaining high-quality soldered joints. Oxide films are removed by the action of gas media, fluxing, ultrasonic treatment, mechanical, or plasma-chemical methods.

When metals are heated in active (reducing) gas environments, such as nitrogen–hydrogen mixtures, hydrogen interacts with the molten solder. However, a drawback of this process is the hydrogen's interaction with the molten solder, leading in some cases to hydrogen embrittlement and the formation of pores, cracks, and other defects.

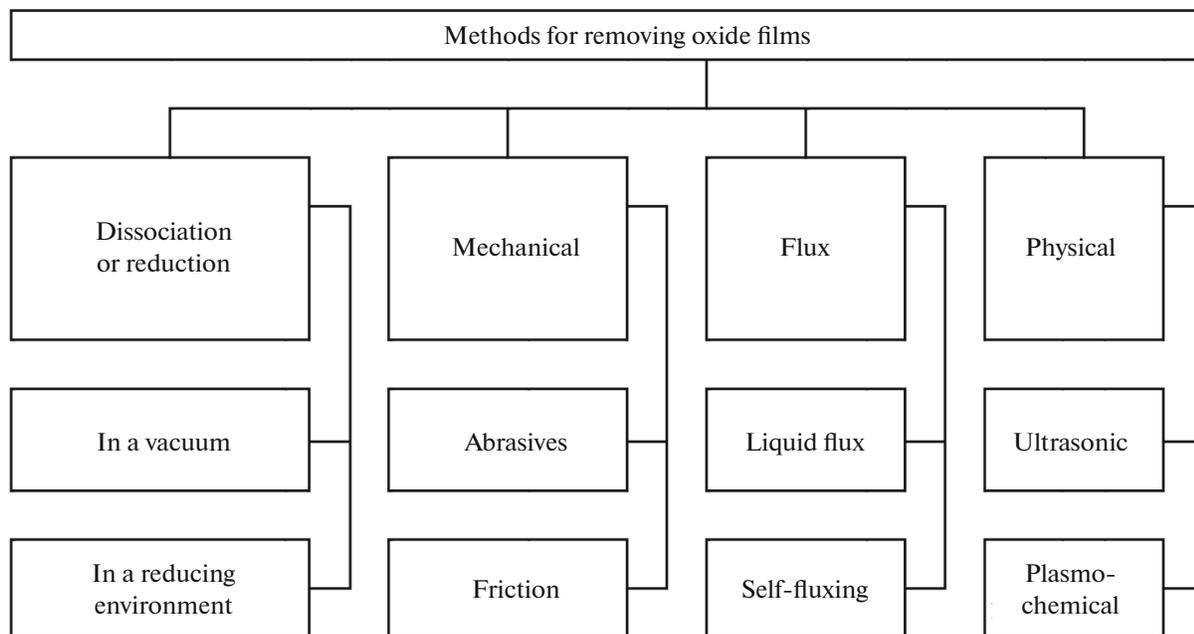


Fig. 2. Classification of methods for removing oxide films.

Dry cleaning methods such as ion, ion-plasma, and plasma-chemical etching enable precise treatment of solderable surfaces in a vacuum, removing not only contaminants but also adsorbed gases. Ion etching is performed by bombarding the surface with accelerated positive ions of inert gases, which transfer kinetic energy to surface atoms. The sputtering of surface atoms occurs when their energy exceeds the interatomic interaction energy in the solderable material. The impact of the ion beam on the metal surface leads to the evaporation of the oxide film in the processing zone. The sputtering coefficient  $K_{\text{sput}}$  depends on the mass of the material  $m_1$ , the mass of the ions  $m_2$ , energy  $E$ , the angle of incidence of the ion beam  $\theta$ , as well as the physical state of the surface [2],

$$K_{\text{sput}} = km_1m_2E/[\lambda(m_1 + m_2)], \quad (3)$$

where  $k$  is a coefficient characterizing the state of the surface, and  $\lambda$  is the mean free path of the ion.

At an argon ion energy of 1 keV, the sputtering coefficient for silicon ranges from 0.6 to 0.8, while for gallium arsenide, it is approximately 1.25. However, ion etching suffers from a low etching rate (0.1–1.0 nm/s) and significant thermal impact on the treated surface.

Plasma-chemical etching uses the energy of the accelerated ion flux of active gases, generated in a vacuum during ion-plasma or magnetron sputtering. The presence of atomic oxygen in the plasma facilitates the effective removal of organic contaminants from the surface and enhances the etching rate. Since the energy of ions does not exceed 100 eV, no physical sputtering of the surface layer occurs. However, a drawback is the high selectivity of etching, which is

due to the chemical mechanism, and the complexity of controlling numerous technological parameters.

To achieve a glowing gas discharge in a sealed chamber, low-frequency (LF), radio-frequency (RF), and microwave (MW) generators are used. LF generators operate in the kilohertz range (40, 80, or 100 kHz) and are employed for rapid “hard” cleaning of plates, substrates, and components from contaminants. RF generators, operating at a frequency of 13.56 MHz, generate a “soft” plasma that does not damage exposed chips in microassemblies. However, these generators need to be matched to the load to increase the incident power and minimize reflection. MW generators operating at a frequency of 2.45 GHz are used to remove thick layers of organic materials, such as photoresists [3].

## 2. REMOVAL OF OXIDE FILMS FROM SOLDERED SURFACES

In the normal state, metal surfaces are covered with oxide films. Heating the base metal and the molten solder leads to a decrease in their activity because of the interaction with oxygen in the air and the growth of oxide films on the surface, the removal of which is a necessary condition for obtaining high-quality soldered joints. The classification of methods for removing oxide films is given in Fig. 2.

The equilibrium constant of the metal oxidation reaction,  $K_{\text{eq}}$ , depends on the partial pressure of oxy-

gen in the surrounding environment at a given temperature [1],

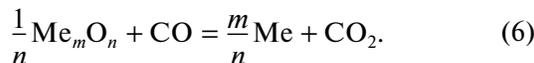
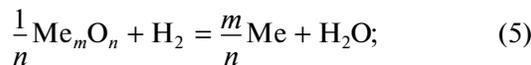
$$K_{\text{eq}} = \frac{P_{\text{met}}^n P_{\text{O}_2}^m}{P_{\text{met}}^m P_{\text{O}_2}^n}, \quad (4)$$

where  $P_{\text{met}}$ ,  $P_{\text{O}_2}$ ,  $P_{\text{metO}_2}$  are the vapor pressure of metal, oxygen, and oxide, respectively.

By reducing the partial oxygen pressure and increasing the temperature of the environment, the equilibrium of the reaction can be shifted towards the decomposition (dissociation) of the oxide. However, complete decomposition of metal oxides (such as tin and copper) occurs at low pressures ( $10^{-6}$ – $10^{-8}$  Pa) and temperatures of 600–700°C. During the soldering of metals in active gas environments, the removal of oxide films from the surface of the base metal and solder occurs through the reduction of oxides by active components of the gas environment, such as hydrogen or carbon monoxide.

This inevitably leads to the interaction of metals with components of the gas environment, as well as with impurities such as oxygen and water vapor. During soldering, hydrogen causes the most harmful effect on the molten solder, as its interaction with the solder flux occurs most actively. The presence of hydrogen in the solder joint can lead to hydrogen embrittlement and the formation of cracks, pores, and other defects. Some metals, such as lead, cadmium, tin, titanium, and zirconium, form hydrides during soldering in a reducing environment, so soldering them in a hydrogen atmosphere is impractical.

When metals are heated in active (reducing) gaseous media, containing a nitrogen–hydrogen mixture or carbon monoxide, metal oxides are reduced by the active components of gaseous media according to the reactions



One drawback of such a process is the interaction of hydrogen with the molten solder, which in some cases leads to the occurrence of hydrogen embrittlement, the formation of pores, cracks, and other defects. The reducing properties of these gases are determined by the concentration of hydrogen or carbon monoxide, as well as the degree of gas purification from water vapor, carbon dioxide, oxygen, and other impurities.

The essence of the mechanical method for removing oxide films from the surface of the soldered metal lies in their destruction under a layer of liquid solder using cutting tools or abrasive materials, with the solder protecting the soldered metal surface from oxygen exposure and coming into physical contact with it. Metallic brushes, meshes, pumice, and metallic pow-

ders are used as cutting and abrasive tools, while abrasive materials are introduced into the solder in finely ground form. Abrasive powders should have lower density compared to the solder to float to the surface.

During mechanical removal of oxide films, solder with a wide melting temperature range, such as tin–zinc alloys (4–50% of Zn), is also used, where the primary crystals of Zn and Sn in the solder can act as abrasives. The process of removing the oxide film is carried out at temperatures below the liquidus temperature but above the solidus temperature of the solder when the primary crystals are separated from each other by the liquid phase. The drawbacks of fluxless low-temperature soldering with abrasive removal of the oxide film include low process productivity, uneven thickness of the solder layer, the presence of unsoldered areas due to difficulties in controlling the film destruction process, and contamination of the solder with abrasive particles.

The processes of fluxless soldering are essential in the assembly of electronic devices and instruments where the use of fluxes needs to be avoided. Flux decomposition products contribute to the development of corrosion processes, which can deteriorate the operational characteristics of semiconductor devices and integrated circuits, as well as affect the reliability and durability of electronic equipment. During the soldering of microstrip boards and silicon chips of semiconductor devices to nonmetallized ceramic substrates, oxide films are removed by the vibrations of one of the joined parts, preferably the upper one, while the second part remains stationary throughout the process.

The lapping process is carried out using installations such as EM-4025, EM-415, and EM-445 (Planar-SO) by transmitting vibrations with a frequency of 1–100 Hz to the joined parts (Fig. 3). During the movement of the soldering surface of board 3, fixed in holder 2, relative to base 5 in a parallel plane using vibrator 1 with an amplitude of up to 1 mm, oxide films on the soldering surfaces 4 are destroyed. The soldering process is carried out without fluxes in the temperature range of 130–610°C for 30–60 s. The strength of the soldered joints is sufficiently high and exceeds the values obtained in the case of soldering in a protective gas environment. Among the drawbacks of the method are the duration of the process, the need to ensure high parallelism of the flat surfaces of the soldered parts, and the effect of vibrations of significant amplitude on the elements.

Fluxing is the most common method of removing oxides during soldering. Flux, as a chemical reagent, serves two primary purposes: to clean the metal surface from oxides and to decrease the surface tension of the solder and the wetting angle.

Typical representatives of active fluxes contain water or alcohols as solvents, while activators include inorganic and organic acids or their salts, such as

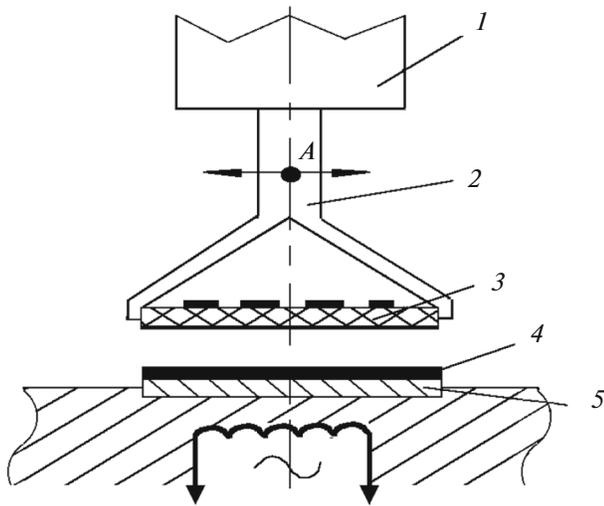
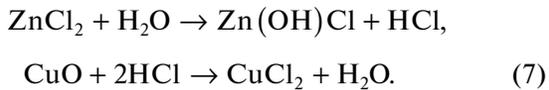


Fig. 3. Soldering with lapping of soldered surfaces.

hydrochloric or phosphoric acid, inorganic salts ( $\text{ZnCl}_2$ ,  $\text{NH}_3\text{Cl}$ ,  $\text{SnCl}_2$ ,  $\text{CuCl}$ , etc.). When zinc chloride interacts with water, hydrochloric acid is formed, which dissolves oxides on the metal surface:



Thus, cupric chloride is formed, which, due to its good solubility in water, needs to be removed from the surface of the component. Since flux based on zinc chloride is highly active, its residues have a corrosive effect and must be thoroughly removed.

Ultrasonic removal of oxide films is based on the introduction of elastic mechanical vibrations with frequencies of 18–45 kHz into the molten solder, creating cavitation, and a series of associated phenomena: sound pressure, micro-, and macroflows. Cavitation is accompanied by the formation, development, and collapse of gas voids in the liquid medium. Real liquids and molten metals contain insoluble impurities, on the surface of which, in cracks and depressions, undissolved gas bubbles with a size of  $10^{-6}$ – $10^{-7}$  m may be present. When ultrasonic vibrations with an intensity of  $10^4$  W/m<sup>2</sup> are introduced into the molten metal, these cavitation nuclei begin to pulsate at the frequency of the vibrations. Their number increases due to the formation of ruptures in the liquid medium at ultrasound intensities exceeding  $2 \times 10^4$  W/m<sup>2</sup> [4].

The dynamics of the development of cavitation voids with a size of  $1 \times 10^{-5}$  m in an ultrasonic field at different ultrasonic intensities are shown in Fig. 4. At an ultrasonic wave pressure of  $2 \times 10^5$  Pa, the expanded cavity collapses, and the concentrated kinetic energy in a small volume is partially transformed into a force pulse and partially into thermal energy. From the center of the collapsed cavity, a

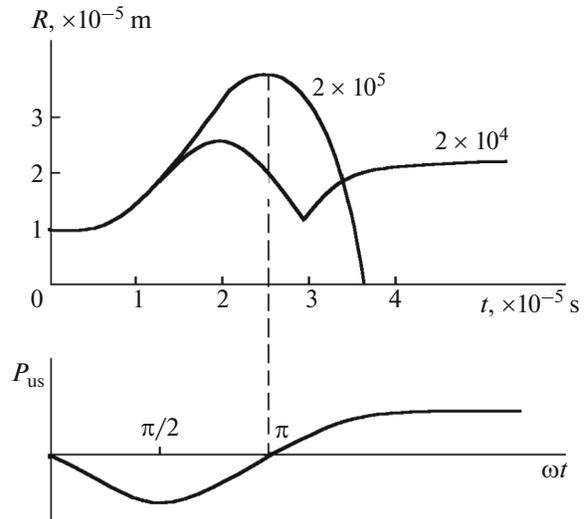


Fig. 4. Dynamics of cavitation voids in a solder melt.

shock spherical wave propagates, with a pressure at a distance  $10R_0$  (according to calculations) reaching 150 MPa, and the temperature exceeding  $1000^\circ\text{C}$ . The destruction of metal oxide films mainly occurs due to cavitation in the liquid solder, while secondary ultrasonic effects contribute to solder mixing and accelerate the tinning process. The collapse of cavitation voids and the creation of microflows in the molten solder lead to the removal of oxide films from the metal surface, enabling the soldering and tinning of difficult-to-solder metals such as aluminum, magnesium, and nickel, as well as refractory metals and alloys based on them.

The detachment of oxide films is caused by high local pressures (up to  $10^5$  MPa) generated near collapsing cavitation bubbles.

The schematic representation of the destruction of oxide film *I* on the surface of aluminum *3* is illustrated in Fig. 5. The directions of the hydrodynamic impacts arising from the collapse of cavitation bubbles are indicated by arrows. The exposed surface of the base metal is uniformly wetted by solder *2* after the removal of the oxide film. The potential mechanism of brittle oxide film destruction involves its fracturing and detachment due to microimpacts occurring during the collapse of cavitation bubbles.

This process has been studied using high-speed cinematography [4]. In cases where the forces of pulsating cavitation bubble oscillations (as shown in Fig. 6a) exceed the adhesion strength between the film and the surface, free film fragments detach from the surface (Fig. 6b). If the strength of the film exceeds the adhesion forces, then the entire film detaches from the surface.

Thus, cavitation and secondary ultrasound effects create the necessary conditions for the wetting of a

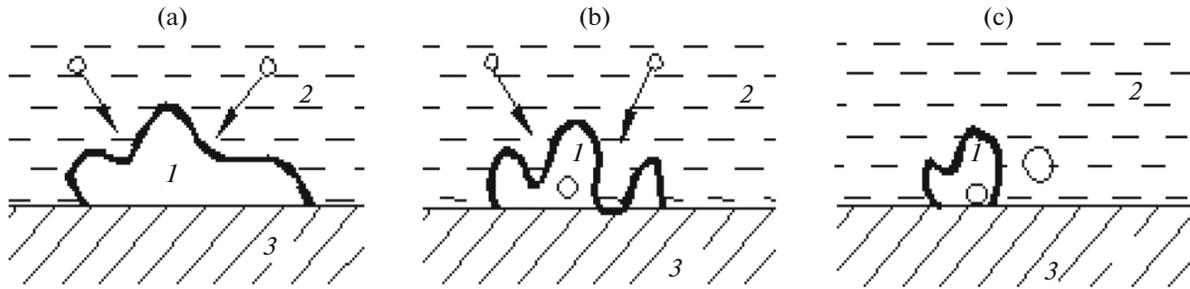


Fig. 5. Sequence of the destruction of oxide films during cavitation.

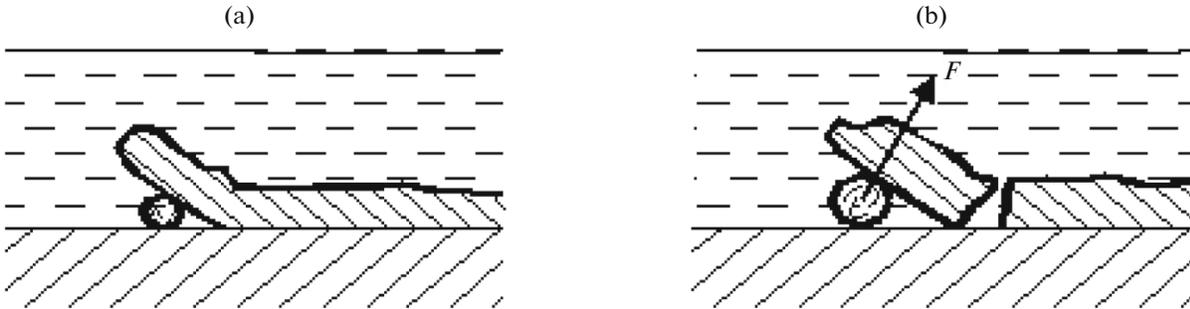


Fig. 6. Schematic diagram of film peeling by pulsating cavitation bubble.

solid surface by molten solder, accompanied by a decrease in the wetting angle and an increase in the spreading factor.

### 3. PROCESSES AT THE SOLDER–SOLDERED SURFACE INTERFACE

The interaction at the base metal–liquid solder interface is associated with the wetting and spreading processes of solder over the soldered surface. The wetting process of the base metal by solder involves replacing the interatomic bonds between metals in the solid phase with metallic bonds of atoms at the interface between them. The interaction of surface tension forces determines the contact angle of wetting  $\theta$  (Fig. 7). The equilibrium condition of the droplet on the sur-

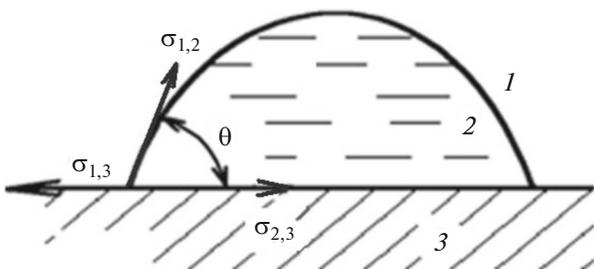


Fig. 7. Schematic equilibrium of surface tension forces: (1) gas, (2) solder, and (3) base metal.

face corresponds to the minimum of the free surface energy  $E_{\text{surf}}$ , which represents the excess energy of surface atoms due to the imbalance of binding forces in the lattice. The change in surface energy is described by the Young’s equation

$$\frac{dE}{dS} = \sigma_{1,3} - \sigma_{2,3} - \sigma_{1,2} \cos \theta = 0. \quad (8)$$

It follows from Eq. (8) that

$$\cos \theta = \frac{\sigma_{1,3} - \sigma_{2,3}}{\sigma_{1,2}}. \quad (9)$$

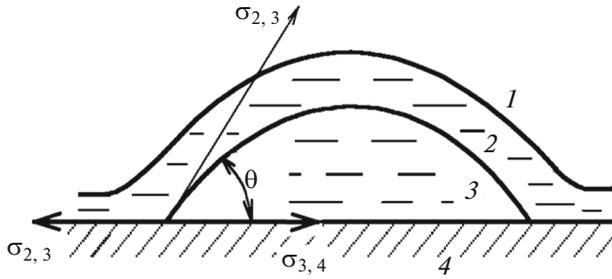
The value of  $\cos \theta$  serves as a parameter for the quantitative assessment of the degree of wetting:

- (1) Complete wetting at  $\cos \theta = 1$  and  $\theta = 0$ ;
- (2) Limited wetting at  $0 < \cos \theta \leq 1$  ( $0^\circ \leq \theta \leq 90^\circ$ ,  $\sigma_{2,3} \leq \sigma_{1,3}$ );
- (3) Nonwetting at  $-1 \leq \cos \theta < 0$  ( $90^\circ \leq \theta < 180^\circ$ ,  $\sigma_{2,3} > \sigma_{1,3}$ ).

The work of adhesion forces  $W_{\text{adh}}$  is associated with the formation of an interphase boundary with energy of  $\sigma_{2,3}$  instead of single surfaces with energies of  $\sigma_{1,2}$  and  $\sigma_{1,3}$ , i.e.,

$$W_{\text{adh}} = \sigma_{1,2} + \sigma_{1,3} - \sigma_{2,3}. \quad (10)$$

To overcome the cohesive forces between particles within the liquid itself (cohesive forces), work must be done against the cohesive forces to create two unit surfaces of the liquid with energies  $\sigma_{1,2}$ , that is,



**Fig. 8.** Schematic equilibrium of surface tension forces in flux medium: (1) gas, (2) flux, (3) solder, and (4) base metal.

$$W_{\text{coh}} = 2\sigma_{1,2}. \tag{11}$$

Taking into account Eqs. (10) and (11), Eq. (9) can be reduced to the form

$$\cos \theta = \frac{2W_{\text{adh}} - W_{\text{coh}}}{W_{\text{coh}}}. \tag{12}$$

Liquid metals and alloys have higher surface tension compared to nonmetallic liquids. For instance, for a SnPb solder,  $\sigma_{1,2} = 0.5 \text{ N/m}$ , which exceeds the surface tension of water by an order of magnitude. In this case, the formation of bonds due to Van Der Waals forces cannot facilitate wetting. To achieve wetting during soldering, high-energy interatomic bonds of a chemical nature with significant adhesion work,  $W_{\text{adh}}$  (metallic, metal-covalent, etc.), must be formed at the interface. Realistic methods to improve wetting involve the use of protective gas environments (reducing  $\sigma_{1,2}$ ) and thorough cleaning of the contacting surfaces of solid and liquid phases from oxide films (reducing  $\sigma_{2,3}$ ).

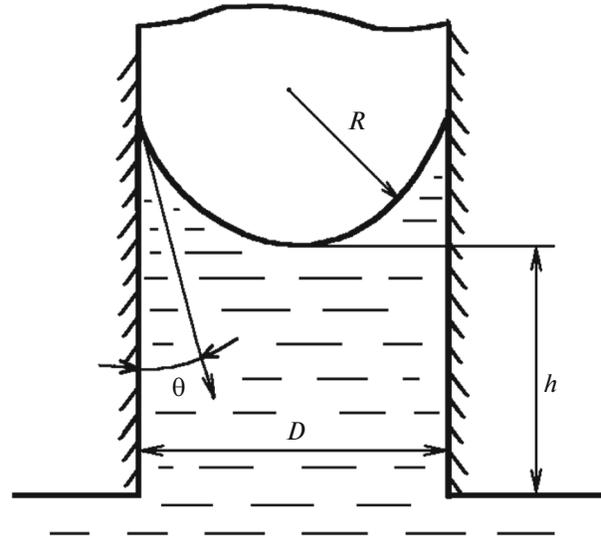
When considering the equilibrium conditions of the solder–base metal system in a flux environment (Fig. 8),  $\sigma_{2,4}$  (interfacial tension at the flux–base metal interface) is introduced instead of  $\sigma_{1,2}$ . In this case,  $\sigma_{2,4} < \sigma_{1,2}$  and  $\sigma_{3,4} < \sigma_{1,3}$ , and the equation for the contact angle takes the form

$$\cos \theta = \frac{\sigma_{3,4} - \sigma_{2,4}}{\sigma_{2,3}}. \tag{13}$$

To achieve wetting in this case, it is necessary to displace the solder by the reacted flux as the oxide film is removed from the surface of the base metal, which is accomplished when  $\sigma_{2,3} < \sigma_{3,4}$ .

When the components of the base metal and solder have sufficient chemical affinity, the energy  $\sigma_{2,3}$  is low, while the work  $W_{\text{adh}}$  is high. In this case, the second wetting condition is satisfied:  $W_{\text{adh}} > \sigma_{2,4}$ .

The solder spreads over the surface of the base metal because of the interaction of surface tension forces; spreading is accompanied by the convergence of the liquid and solid phases. The solder spreading



**Fig. 9.** Liquid rise in a capillary.

factor can be determined from the condition of the ratio of the work of the adhesion and cohesion forces:

$$K_{\text{sp}} = W_{\text{adh}}/W_{\text{coh}} = \sigma_{1,2}(\cos \theta + 1)/2\sigma_{1,2} = (1 + \cos \theta)/2 > 0. \tag{14}$$

Then, with complete wetting,  $\cos \theta = 1$  and  $\theta = 0$ ,  $K_{\text{sp}} = 1$ ; at limited wetting,  $0^\circ < \cos \theta \leq 1$ ,  $0^\circ \leq \theta \leq 90^\circ$ ,  $K_{\text{sp}} = 0.5$ ; at nonwetting,  $-1 \leq \cos \theta < 0^\circ$ ,  $90^\circ \leq \theta < 180^\circ$ ,  $K_{\text{sp}} = 0$ .

#### 4. SOLDER CAPILLARITY AND DIFFUSION

Upon wetting, the solder fills the gaps between the joined parts, forming menisci near the vertical walls and thereby exhibiting capillary properties. The pressure difference acting on the curved surface of the liquid represents the capillary pressure  $p_c$ , determined by Laplace’s equation [5]

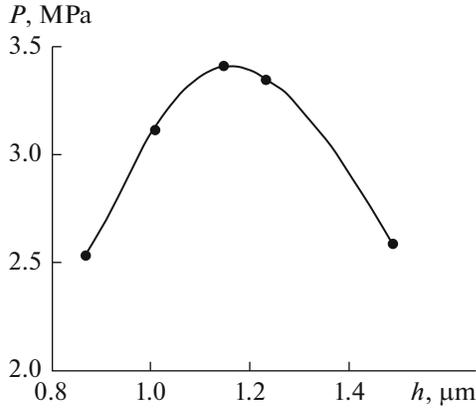
$$p_c = p_1 - p_2 = \sigma_{1,2} \left( \frac{1}{R_1} + \frac{1}{R_2} \right), \tag{15}$$

where  $p_1$  and  $p_2$  are the fluid pressure for convex and concave surfaces, respectively, and  $R_1$  and  $R_2$  are the radii of curvature of surfaces.

For a convex surface,  $p_c$  is considered positive and directed inward into the liquid, while for a concave surface,  $p_c$  is negative and directed outward from the liquid surface. When the capillary diameter  $D$  is small, the free surface of the liquid takes the form of a sphere (Fig. 9) with a radius

$$R = \frac{D}{2 \cos \theta}. \tag{16}$$

Substituting the value of the meniscus radius into Eq. (16), we obtain



**Fig. 10.** Dependence of the strength of soldered joints on the width of the diffusion zone.

$$p_1 - p_2 = \sigma_{1,2} \left( \frac{2 \cos \theta}{D} + \frac{2 \cos \theta}{D} \right) = 4 \frac{\sigma_{1,2} \cos \theta}{D}. \quad (17)$$

The pressure difference  $p_1 - p_2$  is balanced by a solder column of height  $h$ ,

$$h\rho g = \frac{4\sigma_{1,2} \cos \theta}{D}. \quad (18)$$

It follows from Eqs. (16) and (18) that the height of solder rise in a capillary of circular cross-section is proportional to its surface tension and wetting ability and inversely proportional to the diameter of the capillary and the solder density,

$$h = \frac{4\sigma_{1,2} \cos \theta}{D\rho g}. \quad (19)$$

Unlike ordinary liquids, a molten solder represents a system consisting of multiple components, and during its spreading, there occurs a physicochemical interaction among the components and the base metal, dissolution of the base metal in the solder, and interaction with gas and flux media. When displacing flux from the capillary, the height of the solder rise is determined by the equation

$$h_1 = \frac{4\sigma_{1,2} \cos \theta}{Dg(\rho_{\text{solder}} - \rho_{\text{flux}})}. \quad (20)$$

In a horizontal capillary with a width of  $h$  and solder viscosity  $\eta$ , the flow time  $t$  over a length of the capillary  $L$  is determined as follows:

$$t = \frac{6\eta L^2}{\sigma_{2,3} \cos \theta h}. \quad (21)$$

The primary processes governing the interaction between solder and the base metal during the second stage of the physicochemical interaction are diffusion processes. The diffusion process under constant temperature and steady-state substance flow over time is described by the first Fick's law equation,

$$m = -D \frac{\partial C}{\partial x}, \quad (22)$$

where  $m$  is the amount of diffusing substance,  $D$  is the diffusion coefficient,  $C$  is the concentration of the substance, and  $x$  is a coordinate. The minus sign indicates that the diffusion process occurs in the direction of decreasing substance concentration.

Under real conditions, the diffusion rate is a time-varying quantity; therefore, the diffusion process is governed by the Fick second equation,

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2}, \quad (23)$$

where  $\partial C / \partial t$  is the rate of change in the concentration of the diffusing substance.

The diffusion coefficient depends on temperature,

$$D = D_0 e^{-Q/(RT)}, \quad (24)$$

where  $D_0$  is a coefficient depending on the type of crystal lattice,  $Q$  is the activation energy of diffusion,  $R$  is the universal gas constant,  $R = 8.31$  kJ/(kmol deg), and  $T$  is the absolute temperature.

For practical purposes, the solution to the second Fick equation has the form

$$C_x = C_0 \left( 1 - \Phi \left( \frac{x}{2\sqrt{Dt}} \right) \right), \quad (25)$$

where  $C_x$  is the concentration of the diffusing substance at depth  $x$  from the surface,  $C_0$  is the concentration of the substance on the surface, and  $\Phi$  is the integral of the Gaussian error function.

The rate of the diffusion process is affected not only by temperature but also by the condition of the metal. Strain, accompanied by the distortion of the crystalline lattice and the appearance of vacancies, enhances diffusion along grain boundaries and dislocations, leading to an increase in the diffusion zone. Diffusion processes during soldering contribute to enhancing the mechanical strength of joints. However, the formation of intermetallic compounds in the solder, such as  $\text{Cu}_3\text{Sn}$  and  $\text{AuSn}_2$ , due to the deep mutual diffusion of components, affects the strength of soldered joints (Fig. 10).

## 5. SOLDER CRYSTALLIZATION AND FORMATION OF JOINTS

The process of solder crystallization is accompanied by the solidification of the liquid metal layer of the molten metal in the gap. In this process, the change in entropy of the system  $\Delta S$  is the difference in entropies between the liquid and solid states,

$$\Delta S = S_l - S_s = \frac{Q_{\text{fusion}}}{T_{\text{cryst}}}, \quad (26)$$

where  $Q_{\text{fusion}}$  is the latent heat of fusion, and  $T_{\text{cryst}}$  is the crystallization temperature.

The main features of crystallization during soldering are as follows:

- Nonequilibrium nature of the process, meaning there is no composition alignment in the liquid phase, leading to the formation of regions with increased brittleness alongside the low-melting phases of high-melting metals in the solder joint;
- Influence of the base metal in the form of epitaxially oriented crystallization of solder grains near the surface of the base metal;
- Pronounced liquation in the solder joint, resulting in the formation of zonal inhomogeneities and dendritic structures with lower strength;
- Dependence of the crystallization behavior on the volume of solder in the gap.

To obtain reliable soldered joints, eutectic solders with a narrow crystallization zone are used, and the crystallization time is shortened to promote the formation of a fine-grained solder structure. To shorten the solder crystallization time in the joint, inert gas blowing or application of chemically inert, heat-resistant liquids are employed.

Liquation phenomena occurring during the crystallization of solder joints largely depend on the size of the gap in the joint. With relatively large gaps (0.5 mm and larger), the crystallization of most solders occurs with the formation of a well-developed dendritic structure. Under conditions of small gaps (0.3 mm and smaller), layer-by-layer directional crystallization of the liquid alloy takes place.

The crystallization of liquid metal in the solder joint occurs under the orienting influence of the substrate (base metal), where the grain boundaries of the solder within the crystallization zone continue the grain boundaries of the base metal. Oriented crystallization in solder joints is most characteristic when the solder and the base metal share a common metallic basis or have the same type of crystal lattice.

The physicochemical interaction between the solder and the base metal results in a soldered joint with a specific structure. The solder joint includes a melting zone (solder) and diffusion zones at the interface between the solder and the base metal (Fig. 11). The final structure and composition of the soldered joint depend on the nature of the interacting metals, their chemical affinity, and the time and temperature of soldering. The following types of joints are distinguished:

- *Nondiffusion joint.* No diffusion zones can be detected by existing analysis methods. Such joints form between metals with weak chemical affinity, low mutual diffusion coefficients, short soldering times, and limited temperature ranges (e.g., Fe–Sn);
- *Solution-diffusion joint.* The reacting components form solid solutions or intermediate phases

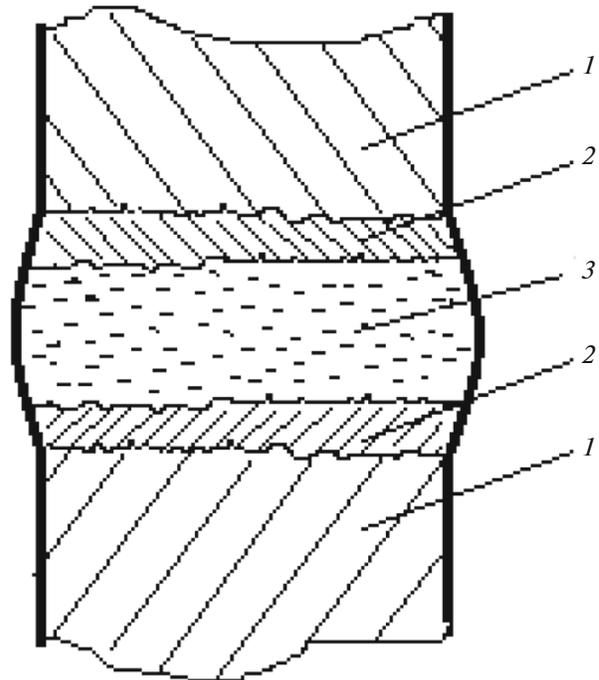


Fig. 11. Structure of a soldered joint: (1) joined metals, (2) diffusion zone, and (3) solder.

(intermetallic compounds), such as Au–Sn, Ag–Sn, and others;

- *Contact-reaction joint.* This type of bond occurs when a metal contacts a semiconductor, resulting in the formation of a eutectic alloy with a low melting temperature (e.g., Au–Si).

In the case of a nondiffusion joint, its strength is determined by the free energy of atoms at the interfacial surface, which depends on the degree of crystalline misorientation of the base metal and the nature of the bonding energy. The strength of such a joint is greater with a higher degree of surface cleanliness of the base metal and the purity of the surrounding environment.

In solution-diffusion joints, continuous or limited solid solutions, eutectics, and intermetallic compounds may form. Dissolution of the base metal into the solder alloy during melting leads to the precipitation of excess phases during the solidification of the solder joint. Uniform distribution of components in the solder joint under conditions of solution-diffusion bonding can be achieved with very small clearances in the joint (less than 0.1 mm). Such a joint structure is characterized by high joint strength.

The highest mechanical strength is exhibited by lap and butt joints with overlays, while stepped joints ensure enhanced precision (Fig. 12). It is important to ensure the preliminary fixation of the components during assembly. Various methods are used for component fixation, including pin connections, tack weld-

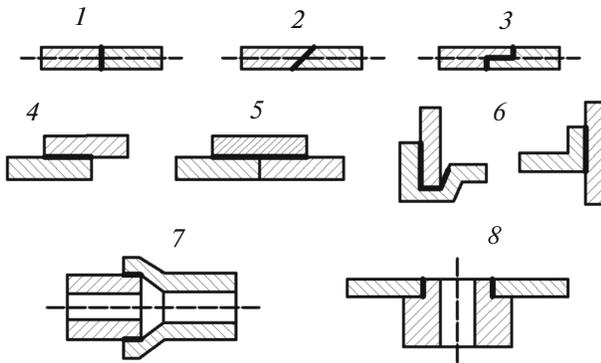


Fig. 12. Types of structural soldered joints: (1) butt joint, (2) lap joint, (3) stepped, (4) overlap, (5) overlay, (6) lock, (7) telescopic, and (8) flanged tube.

ing, crimping, flanging, spot welding, swaging, special structural elements (sockets, recesses, flanges), etc. Components used in the assembly must meet the requirements for manufacturability and have small-diameter holes (0.5–1.5 mm) in closed volumes for the release of air and gases during soldering. Flange joints should have technological allowances of 1–2 mm in length to improve galling formation conditions and to ensure good solderability coating.

The second most important requirement is sufficient mechanical strength, which, depending on operational loads, should be determined by calculation based on the peel resistance. During the design of a soldered joint, it is taken into account that the tensile strength of the soldered joint should be equal to the tensile strength of the weakest component of the structure [7].

$$\sigma_{\text{solder}} S_{\text{solder}} = \sigma_m S_m, \quad (27)$$

where  $\sigma_{\text{solder}}$  and  $\sigma_m$  are the strength limits of solder and material, and  $S_{\text{solder}}$  and  $S_m$  are the cross-sectional areas of solder and material.

The  $\sigma_m/\sigma_{\text{solder}}$  ratio, referred to as the strength coefficient  $\beta$ , is typically greater than unity, hence the effective cross-sectional area of the soldered joint should be several times larger than the cross-sectional area of the base material. From the condition of equal strength (Eq. (27)), the length of the overlap is selected to be equal to two to five times the thickness of the thinnest of the joined parts. The mechanical strength of the joint in a butt joint connection is [8]

$$F_{\text{strength}} = \sigma_{\text{solder}} hb, \quad (28)$$

where  $h$  is height, and  $b$  is width.

In the case of an oblique seam, the joint strength is higher,

$$F_{\text{obl}} = \sigma_{\text{solder}} \frac{h}{\cos \alpha} b, \quad (29)$$

where  $\alpha$  is the bevel angle.

The telescopic connection strength is determined as

$$F_{\text{tel}} = \sigma_{\text{solder}} \times 2\pi RL, \quad (30)$$

where  $R$  is the radius of the covered element.

In the design of soldered joints, optimal clearances between the surfaces of mating assembly elements should be maintained, determined by the composition of the selected solder and the characteristics of the soldering process.

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## CONFLICT OF INTEREST

The authors of this work declare that they have no conflicts of interest.

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