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LEAD FREE THICK FILM CIRCUITS

Selim Achmatowicz[1], Elżbieta Zwierkowska[1]

Distribution of lead in thick film circuits has been indicated. Two categories of lead containing materials, ceramic and metallic, have been distinguished. A short history of removing lead oxides from ceramic materials has been presented. Metallurgical reactions between solder and thick film material, during the soldering and after the joint solidification have been discused. Diverse courses of soldering process of thick film layers and cupper layers of printed circuits have been compared. Useful lead free alloys for soldering lead free thick film have been presented.

1. INTRODUCTION

A great attention of numerous consortia, individual companies and research institutes has been paid to the problem of lead free materials used in electronics. However, those experimental works have been addressed almost exclusively to PCB and thin film assembly. Another type of circuit board assembly that has not received significant attention regarding lead free solder replacement strategy have been thick film hybrid circuits. A limited interest towards implementing lead free soldering into hybrid circuits is due to a relatively small volume of the hybrid circuits within the electronic market.

Thick film technology (TFT), that is the base technology in manufacturing hybrid circuits, belongs to the family of additive technologies of manufacturing microelectronic circuits. The conductive, resistive, cross-over, dielectric, etc., layers are one after the other screen printed onto ceramic substrate. Screen printing is the major feature of TFT. Deposition of each layer requires drying and firing, after screen printing. The main stream of thick film technology applies alumina as the substrates, and firing process with peak temperature at 850°C. Other substrates are also used (BeO, AlN, porcelain-on-steel, glass, ceramic capacitor dielectrics, law temperature co-fired ceramics - LTCC, etc.), and need to be processed according to their individual properties. Thick film technology requires special materials in form of screen-printable pastes (inks). The pastes are composed of minute particles

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[1] Instytut Technologii Materiałów Elektronicznych, ul. Wólczyńska 133, 01-919 Warszawa, e-mail: Selim.Achmatowicz@itme.edu.pl

of suitable materials suspended in an organic vehicle, which is later removed by drying and firing.

Another branch of thick film technology uses materials cured at low temperatures. In this case organic substrates are employed (most common polyesters) together with so called polymer thick films (PTF). The high temperature process cannot be applied, here. Polymer thick film pastes are designed in the way that they do not need firing (sintering). Curing in temperature below 200°C or UV light enables them to perform as conductive, resistive and dielectric layers. This kind of TFT has been successfully employed in many applications (soft switches, electroluminescent lamps, single-use sensors, "jumpers" aiding printed board circuits, EMI shielding, etc.). However, this branch of TFT is not related to lead free problems, therefore will not be presented in this paper.

It has not been widely recognized that thick film circuits (TFC) were the source of lead other than metallic Pb present in the soldering alloy. Actually, the traditional TFCs have been „stuffed" with Pb containing materials. In this paper, these materials are named „ceramic type", since they contain lead oxides in form of glasses or crystallizing glasses.

Figure 1 presents a scheme of a cross-section of thick film circuit indicating where lead may be found.

Section A. Hybrid circuit termination
Section B. An attached component
Section C. A protected resistor
Section D. A cross-over (multilayer)

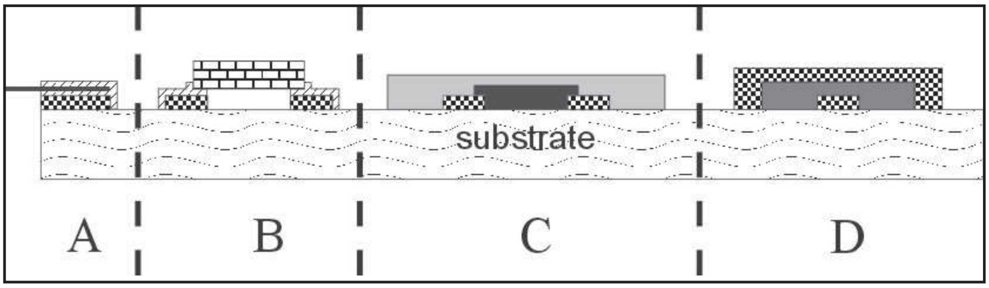


Fig. 1. A scheme a cross-section of TFC showing the sits where Pb may be present:
Rys. 1. Schemat przekroju układu grubowarstwowego wskazujący miejsca obecności Pb:

▩ - conductive layer (warstwa przewodząca),
▓ - resistive layer (warstwa rezystywna),
▒ - dielectric, cross-over layer (warstwa dielektryczna lub skrzyżowanie),
░ - protective layer (element dyskretny),
▦ - discrete component (lutowie),

▨ - solder (lutowie)
▬ - termination wire (wyprowadzenie drutowe)
⬚ - substrate (podłoża)

The statement that all the layers may contain lead is rather safe, as long as the traditional thick film materials are considered.

Conductive layers are composed of sintered metal particles adhered to the substrate with an aid of a glass (frit). In most cases the latter contains lead. The content of lead in the conductive layer may reach the level of up to 5% wt.

Resistive layers are composed of sintered, electrically conductive particles and a glass. The content of lead in the resistive layer may reach a very high level up to 60% wt, due to the high content of lead in the glasses, high content of glasses in the resistive layers, especially those of high resistivity, and presence of lead in some conductive material, such as $Pb_2Ru_2O_{6.5}$.

Dielectric layers shown in the picture represent cross-over. Other layers such as multilayers, thick film capacitors, etc., are of the same nature, in respect of lead content. They all may contain lead on a varying level from a few % up to 40% wt.

Protective layers which provide environmental (e.g. humidity) and process (e.g. trimming) protection, mostly for resistors, fired at lower temperature 600-650°C, are a serious source of lead which may be even over 50% wt.

Components (IC chips, inductors, capacitors, transducers, sensors, etc.) are not necessarily free from lead.

Solder layers are the main source of the metallic lead. A very common content of lead in SnPb solders is 34-37% wt.

Terminations may contain lead if coated with SnPb finish.

Substrates in general are free from lead. However, LTCC, porcelain-on-steel, some glasses may contain lead.

It becomes obvious that removal of toxic ingredients from thick film circuits substituting them with some other materials has been a serious task, completely different in case of "ceramic" lead as that of metallic lead.

2. RELATION BETWEEN THICK FILM TECHNOLOGY AND SOLDERING

Thick film technology, as many people believe, has been a proprietary art since some 50 years. R. W. Vest, in his fundamental publication „Material science of thick film technology" [1], explained majority of material aspects related to TFT, making an attempt to convert the art of thick films to a science.

Thick films are very complex, non-equilibrium systems related to their microstructure determined by the combination of material properties and processing. Most thick film pastes contain some active ingredients, glass (a permanent binder) and screening agent (organic vehicle – temporary binder). For conductors, the active ingredients are metal or metal alloy powders; for dielectrics, the active ingredients are glasses, glass ceramic or inorganic oxides; for resistors, they are highly conducting oxides, nitrides, silicides, or borides; and for thermistors, the active ingredients are semi-conducting oxides. The permanent binder, which is added to provide adhesion to the substrate, quite often influencing the electrical properties of the given layer, is glass frit or an inorganic oxide powder. The organic vehicle is a resin or a polymer (e.g. ethyl celluloses) in a suitable solvent of a relatively high boiling point (e.g. terpineol, butyl cabitol).

Printing ability of thick film pastes has to meet several requirements. It should have a low viscosity at high shear rates, produced when the squeegee traverses so that paste transfer to the substrates is effective. Since the printing is through the screen, the viscosity should remain low for a short time so that printed film can level. Soon later, the viscosity of the paste should increase rapidly, to avoid bleeding out. The other major requirement for the component of the organic vehicle is that they should be removable completely in the course of the firing process. In addition they should not influence the chemistry of the inorganic ingredients of the paste before they are removed.

The role of glasses (frits) and crystallizing glasses varies depending on their location in the circuit. There are certain general properties that these glasses should possess: high electrical resistivity, thermal shock resistance, low dielectric constant and dielectric loss, environmental inertness, etc. In addition, there are several physical properties of the glass that should have proper value for the given application – selected substrate or attached component(s). Thick film glasses are typically borosilicates with intermediates and modifiers such as: Al_2O_3, Bi_2O_3, PbO, CdO, ZnO, BaO and CaO. The high lead glasses were most common, before the ban on lead have been announced, e.g. with a composition: 63 wt% PbO, 25 wt% B_2O_3, and 12 wt% SiO_2. It has a thermal coefficient of expansion very close to alumina and appropriate viscosity and surface tension for firing in the range 800 to 900ºC [1]. Lead oxide has unique, dual properties at the some time being modifier and glass forming oxide. For many years it has been regarded as a perfect material to be employed in thick film materials. Lead oxide was very useful in designing glasses with desired thermal coefficient of expansion and/or thermal properties (softening and melting point, etc.), necessary for good compatibility of the layer and the applied substrate.

A thorough review of properties and behavior of the layers resulted in consequence of the use of thick film pastes is beyond the scope of this paper. However, it is necessary to concentrate on those properties of the layers which are directly related to the soldering process.

Interaction between a layer and a solder may be of a physical or of a chemical nature. A layer immersed in a molten solder undergoes a thermal shock. A mismatch of the thermal coefficient of expansion, wherever with a thick film circuit occurs, may be critical. Integration of the circuit is in jeopardy. A chemical interaction between layers occurs when the molten solder reacts with the ingredients of the layer, e.g. producing intermetallic compounds. Obviously, the latter concerns the conductive layers only, where metals responsible for conduction, such as Ag, Pd, Pt, Au or Cu may react with metals present in the solder. Somewhere between physical and chemical interactions are properties of conductive layers responsible for wetting, wetting angle and solder leaching. These properties, belonging to physical phenomena, depend very much on chemical as well as physical state of the surface exposed to the solder.

Silver is a very common ingredient of thick film conductors. However, it suffers two major drawbacks: silver tends to migrate in the presence of moisture and an electric field, and is readily soluble in solders of high content of tin. Both problems can be reduced by alloying Ag with 10 to 30% Pd. However, the alloying causes unwanted increase of resistivity and problems of Pd oxidation during the firing. The presence of palladium oxide on the surface of the conductive layer reduces the wetting, thus is harmful to the soldering process. Platinum can be also alloyed with silver to reduce silver migration and solder leaching. In addition, lower level of Pt is required (1-3%) and it does not produce oxidation problems. The choice between Ag/Pd or Ag/Pt alloy is made on the economy bases.

Other than conductive thick film layers are not that much susceptible to chemical interaction with a solder. However, a conflict of thermal coefficient of expansion may be responsible for propagation of micro-cracks. These in turn are critical to electric properties of dielectric layers - causing shorts in cross-over or multilayer structures, as well as for resistive layers – causing difficult to predict drift of resistivity and/or thermal coefficient of resistance (TCR).

Standard procedure of testing thick films includes [2]:

- adhesion, adhesion after ageing, leach resistance for conductors,
- resistance drift, TCR changes after thermal shocks for resistors,
- dielectric constant, dissipation factor, insulation resistance, breakdown,
- voltage for cross-over, multilayer (capacitors, thermistors, etc.)

As it was mention before properties of thick films depend on properties of the ingredients contained in the pastes and the process of their formation. No doubt the firing process is the crucial one, most responsible for adhesion. There are three primary ways to achieve adhesion between a film conductor and the substrate. These are frit (glass) bonding, flux bonding, and reactive bonding. For reactive-bonded films, a very small amount of reactive oxide such as CuO or CdO is added to the paste.

During the firing, these oxides react with the alumina substrate to form a copper or cadmium spinel ($CuAlO_4$ and $CdAlO_4$, respectively) which provides adhesion to the metal film. Flux bonding involves the addition of larger amount of oxide (1-5%) which forms a liquid phase with the substrate at the firing temperature. Bismuth oxide is commonly used because Bi_2O_3-Al_2O_3 eutectic temperature is 820ºC, and transient liquid is formed when the conductor is fired above this temperature. Since in most cases this transient liquid wets to some extent the metal particle, a good adhesion is produced. The third and most common method is frit bonding. 2 to 10% of glass powder is added to the paste. During the firing the glass melts, wets the substrate and penetrates the metal structure, causing of its majority to migrate to the conductor/ceramic substrate. Under such circumstance, glass creates adhesion between the metal particles and the substrate. At the same time sintering of the metal particle occurs.

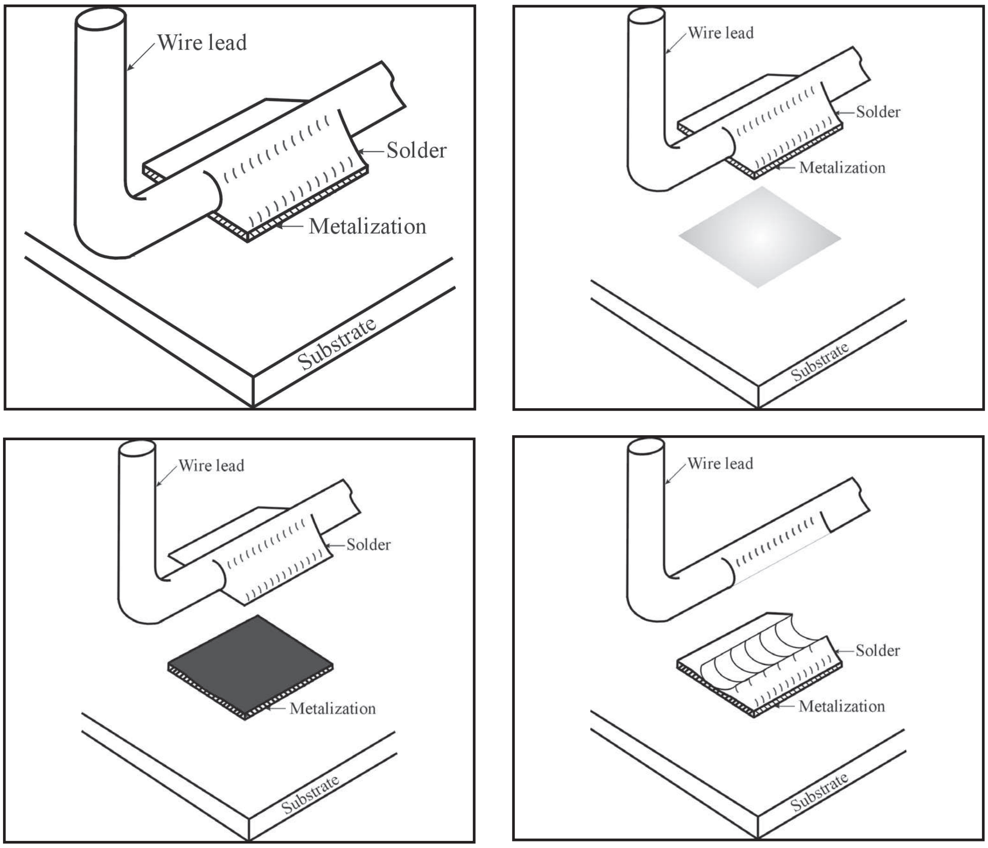


Fig. 2. Adhesion test – various modes of failure during the peel test.
Rys. 2. Badanie adhezji – warianty możliwych uszkodzeń.

The high temperature firing conditions have a significant effect on the extent of metal powder sintering- thus, porosity of the layer as well as presence of glass traces on the surface of the conductive layer. Subsequent soldering process depends very much on the final state of the conductive layer. One of a very significant measure of successful firing is the adhesion of the conductive layer to the substrate. Soldering of the conductive layer, well described in [3], is the most common way to measure adhesion of the conductive layer to the substrate. A peel test consists of attaching a wire to the conductive layer by a solder, and then pulling the wire until it is disconnected from the layer. The necessary force to get the disconnection is the measure of the adhesion. There are three possible modes the wire could be separated from the layer (Fig. 2):

1. the wire is lifted together with the solder and the conductive layer (top right),
2. the wire is lifted just with the solder (bottom left),
3. the wire is pulled away without the solder (bottom right).

The case 1 means that the weakest part of the structure is at the interface of conductive layer and the substrate. The measured value corresponds directly to the adhesion of conductive layer to the substrate. It is believed that one of the main causes of that type of solder joint failure is diffusion of Sn down to the thick film/ substrate interface.

The case 2 means that adhesion of the conductive layer to the substrate is higher than the obtained value of measured force. One of recognized reasons of such failure is excessive growth of intermetallic compounds at the solder/thick film interface.

Same concerns the case 3, however, it also indicates that the soldering process was carried improperly (e.g. incorrect selection of the soldering temperature) or inadequate compatibility between the wire and the solder (e.g. oxidation of wire surface).

There are several methods applied to determining adhesion. The most popular method in thick film technology is the above described peel test. The other one is based on measuring the shear force necessary to remove the component mounted on top of the circuit. The later one is very common in PCB technology. Both testing methods, apart from being the measure of the adhesion of thick film to a substrate, are very valuable in evaluation of solder joints quality.

3. THICK FILM MATERIALS FREE OF „CERAMIC” LEAD

Originally, the driving force to get rid of lead oxide contained in thick film circuits was purely technical, at that time not related to environment protection regulation.

Copper thick film conductors have been of considerable interest as early as the end of ‘70ies. They could bring a substantial cost savings. Copper does not migrate. Being easily solderable is relatively resistant to solder leaching, does not require any expensive alloying. Therefore copper thick film conductors have much higher electrical conductivity than the practical noble metal alloys. However, copper's high affinity to oxygen makes that the conductors cannot be fired in air atmosphere. Commercial copper conductors are fired at 850ºC (or above) in nitrogen with, strictly controlled, residual level of oxygen (1 – 10 ppm). Products of decomposition of organic polymers are present in the furnace, which are very powerful reducing agent. Under such condition lead and bismuth oxides contained in glasses are converted partially to metallic lead and bismuth [1]. This in most cases causes entire lost of metallization adhesion to a substrate.

The liberation of free metals causes also serious problems in case of resistive, dielectric and protective layers. The appearance of a new conductive material – free Pb, within the resistive layer makes that its resistance and TCRs are entirely out of control. The dielectric layers containing metallic inclusion are of no use at all. No surprise that a new set of Pb free glasses had to be elaborated. The employed glasses have been usually borosilicates modified with ZnO, CaO, BaO, MnO, CuO, Al_2O_3, ZrO_2 [5–7].

Another technical reason requiring removal of lead from the pastes composition appeared with the advent of aluminum nitride (AlN) substrates. A very attractive property of AlN substrates is their high thermal conductivity – 140-200 W/m*K. Alumina substrates are composed of an extremely inert aluminum oxide. It is not the case with the aluminum nitride. AlN substrates can stand firing at high temperatures (850ºC) in air atmosphere. However, their resistance to even moderate oxidizing agent is low. Glass containing lead oxide may react with AlN substrate according to the following equation:

$$3\,PbO_{(glass)} + 2\,AlN_{(substrate)} \rightarrow Al_2O_3 + 3\,Pb + N_2\uparrow \qquad (1)$$

damaging the integrity of the circuit [8-9].

A danger of similar reaction to that presented in equation (1) may occur between ruthenium dioxide and AlN:

$$3\,RuO_2 + 4\,AlN \rightarrow Al_2O_3 + 3\,Ru + 2\,N_2\uparrow \qquad (2)$$

The resistive pastes presented additional problem.

A great number of publications and patents have been devoted to find suitable solution of the above problems [5–11]. Some of the publications were oriented towards elaborating lead free glasses. The other authors were searching for lead free active ingredients of the resistive layer (e.g. $CaRuO_3$).

The research conducted to achieve technical benefits became a very useful base to satisfy present environmental regulations. Very intense, recent efforts on eliminating lead and other banned toxic substances, from the compositions of thick film materials resulted in a very broad of all kinds offer of lead-free pastes. Examples of WEB sites of leading pastes manufactures who present most thorough offer of that kind of materials are listed under [4]. Almost all of these pastes, except of being lead-free, are also free from cadmium and nickel derivatives.

4. THICK FILM MATERIALS FREE OF METALLIC LEAD

Thick film technology being the younger sister of PCB technology, also in respect of production capacity, has been taking advantage of experience gained in the process of investigating soldering of copper on laminate and related structures. This was the case at the time when SnPb solders were dominating in electronic assembles, and continues with the advent of lead-free solders. Numerous research results on soldering of copper can be found in the literature, as well as information coming from manufactures of both: solders and assembles. If one goes through the published information on soldering of thick film circuits will hardly find one-tenth of that what is available on copper soldering. Furthermore, solders vendors give their very through recommendation on particular solder application saying nothing about solders for thick film applications. Tab. 1 shows one of such examples [12].

Table 1. Alloy applications [12] (modified).
Tabela 1. Zastosowania stopów lutowniczych [12] (zmodyfikowano).

Alloy Composition	Liquidus, °C	Primary Application	Pot Temp. Range, °C
Sn37Pb	183		232-271
Sn3.5Ag	221	SMT/Wave	260-276
Sn0.7Cu	227	Wave/Semiconductor	265-276
Sn4.0Ag0.5Cu Sn3.0Ag0.5Cu Sn3.0Ag0.7Cu	215-218 215-218 215-218	SMT/Wave/Semiconductor SMT/Wave/Semiconductor SMT/Wave/Semiconductor	271-276 271-276 271-276
Sn2.5Ag1.0Bi05.Cu	215	SMT/Wave	271-276
Sn2.5Ag0.75Cu0.5Sb	214-217	SMT/Wave	271-276

It is believed that comparison of the structures of copper on laminate with thick film layers on ceramic substrate, and the nature of the soldering processes will be a very useful in further consideration.

Copper on a laminate and thick film on a ceramic substrate is very much alike. Both layers are situated on dielectric substrates and metallic, relatively well wetted by most of solders. However, they are far from being identical. Their chemistry is different, and what is even more important, their structure and morphology differs substantially.

The origin of copper in PCBs or in semiconductors assemblies is either Cu foil or Cu deposited on the substrate by electroless or electrolytic plating. The layer manufactured by either method is a solid, dense almost free from porosity, continuous, wrought-like metal. The metal layer is composed of small crystallites closely attached by so called bridge atoms which do not belong to the crystalline lattice of either crystallite. The bridge atoms, forming boundary between crystallites, are relatively rich in energy, thus are pliant to movements. The crystallites boundaries have a great impact on diffusion process, mass transfer during the soldering process, as well as in the solid state. This type of diffusion is called boundary diffusion.

Thick film conductive layer is, as it was already mentioned, made by the sintering process of small size particles of metal(s). There is also present a small fraction of a glaze. The sintered layer consists of lager grains. The morphology of the individual grain is similar as in the copper layer described above. However, most thick film conductors are composed of more than one metal, with silver being the most popular one. In PCB conductive layer the crystallites are composed of one element – Cu. Thick film layers are chemically more complex. This complexity has great influence on future diffusion during the soldering process. The structure of the layer, which is very far from being homogenous, is even more important in respect of diffusion processes. Apart from the boundaries within the grains the sintered grains have large free surfaces (a sharp free boundary). The latter property of the sintered layer is a source of another kind of mass transfer, related to free surface diffusion. The sintered layer is relatively porous. Fig. 3 shows the difference in the structure of thick film layer (the area in between two white dotted lines) and copper layer.

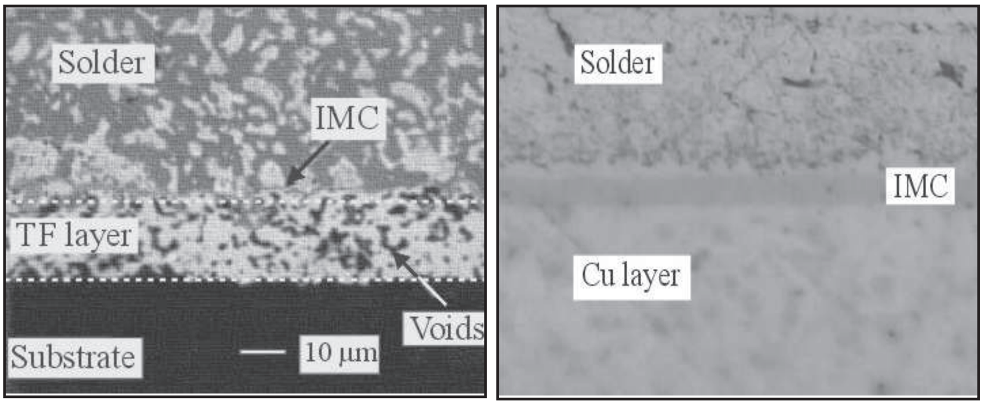


Fig. 3. Cross-section SEM picture of soldered thick film conductive layer (left) compared with soldered copper layer (right).
Rys. 3. Porównanie przekrojów polutowanej przewodzącej warstwy grubej (po lewej) z polutowaną warstwą miedziową obwodu drukowanego (po prawej) – obrazy SEM.

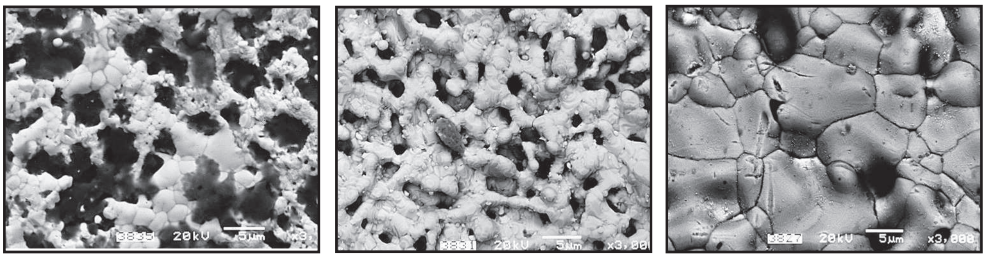
4.1. Wetting and solder leaching

Wetting is the first act of soldering process. It is a very important phenomenon that determines spreading of the molten solder on a conductor surface. It can be quantified as a wetting angle (φ). The wetting angle of molten tin against diverse metal surfaces is relatively low. The solders of high tin content have excellent wetting to noble metals such as Ag and Au, and to a lesser extent Pd and Pt. Wetting occurs simultaneously with chemical reaction between the molten solder and metals contained in the soldered conductor. Too good wetting may cause higher level of conductor layer consumption (solder leaching) that is dissolving it and making the layer thinner. Dissolution of the conductor layer may lead to separating the layer from the substrate called dewetting. Pure Au thick film layers are regarded non-solderable due to their ease to be entirely dissolved in tin reach solders. The excessive solder leaching can be inhibited. The natural way of inhibiting the solder leaching is formation of intermetallic compounds (IMC) which in many instances slow down diffusion in either direction (metal into the solder, solder components into the conductive layer). In thick film technology addition to gold certain metals (Pd, Pt) may be beneficial. Using Au/Pd/Pt alloys is the common way to convert Au thick films into solderable layers. The presence of glassy inclusions may also limit penetration of conductive layer. Still the dominant factor in thick film soldering is the channel like structure of the layers that has great impact on accelerating surface diffusion.

In general, wetting problems are rather related to the structure of soldered conductor. Bochenek et al. [13] gave a very convincing example of soldering dependence of layer structure. Wetting angle (φ) was measured for Ag conductors made of pastes coming from three different vendors (A, B and C). The time of leaching out (t) the layers was determined as well. Small pieces (0.2 mm^3) of 63Sn37Pb solder were placed on silver pads with an addition of the flux. The reflow temperature was 240°C. The time of the reflow was within 5 seconds. Fig. 4 shows SEM picture of the layers surface.

The wettability is assessed well if $\varphi = 0° - 45°$, poor if $\varphi = 45° - 75°$, and very poor or no wettability if $\varphi = 75° - 180°$. The pictures clearly show the way the silver particles are sintered. The surface of the layer A contains numerous inclusions of glass and porosity. The layer C is well sintered, tight, with the surface almost free from inclusions. This proves how much soldering depends on formulation of the paste and the state of the surface of the layer made of that paste.

Wetting angles (φ) of several combinations of solder/thick film are given in Tab. 2. Silver is well wetted by majority of lead-free solders. Addition of antimony makes the solder more complex, however does not improve the wettability of silver. Silver bearing thick film conductors may vary in respect of wettability. The use of Ag/Pd alloys as a conductive phase in thick film conductors leads to a slightly lager wetting angle. However, it should not excide 45°.



A. φ = 180°; t < 1 s **B.** φ = 45° ±4°; t < 1 s **C.** φ = 28° ±2°; t > 180 s

Fig. 4. SEM images of Ag layers made of pastes from three vendors [13]
φ - wetting angle; t – time while the layer is leached out by 63Sn37Pb solder.
Rys. 4. Obrazy SEM warstw Ag uzyskanych z past trzech różnych dostawców [13]
φ – kąt zwilżania, t – czas narażenia warstwy na działanie lutowia 63Sn37Pb.

Table 2. Wetting angle (φ) of several solders against selected thick films.
Tabela 2. Kąt zwilżania (φ) warstw grubych przez różne lutowia.

Substrate	Reflowed Alloy Pellet (Sn +)					
	0.5 Cu	3.5 Ag	3.8Ag 0.7Cu	3.5Ag 0.5Sb	3.8Ag0.7 Cu0.5Sb	37Pb
Cu	42	43	43	41	43	12
Ag	19	26	24	30	33	13
Sn37Pb	19	19	22	20	22	5
Sn0.7Cu	15	11	18	11	10	17
Au/Ni	9	6	10	14	5	4

Wetting rates and spread of Pb-free alloys are satisfactory for thick film technology. Surface tension of lead free alloys is higher than SnPb causing less spread and greater tendency towards tombstones and voids. However, the latter drawback does not seem to be critical. Wetting speed for SnAg and SnAgCu alloys is acceptable at lower superheat temperatures than SnCu alloys.

The higher concentration of tin may also influence solder leaching ability of lead-free solders. Molten tin is known as a very good solvent for many metals – especially silver, and even more gold. Solder leaching at elevated temperature might be very harmful to silver bearing thick film conductors.

An original method for evaluation of the solubility of silver in the molten solder has been presented by Bober et al. [14]. It is based on measurement of cone length formed at the end of silver wire which has been gradually dipped in the molten solder. The results of these tests are presented in Fig. 5.

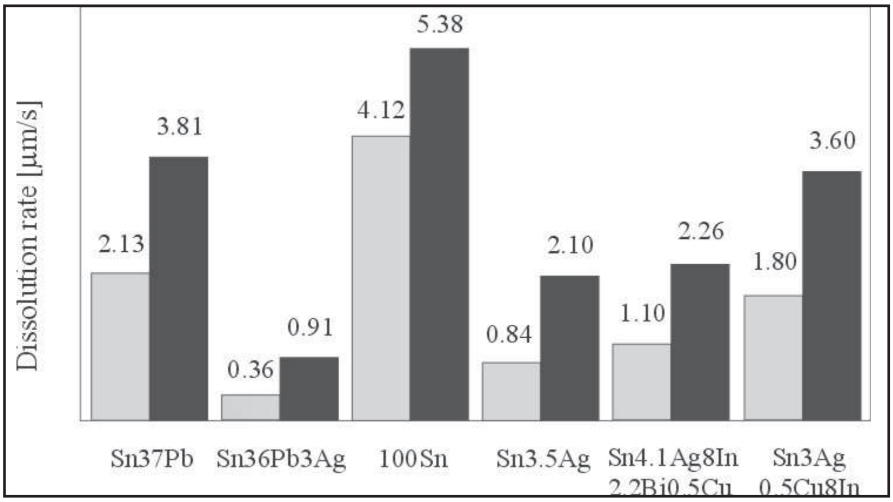


Fig. 5. Dissolution rate of Ag wire in diverse solders. Dipped at 240°C – gray, at 260°C – black [13].
Rys. 5. Szybkość rozpuszczania drutu Ag w różnych lutowiach. Temperatura zanurzania: 240°C - kolor szary, 260°C – kolor czarny [23].

Molten pure tin has the highest rate of Ag solubility. Ag dissolves in 96.5Sn3.5Ag solder at the rate suitable for soldering thick film circuits. Elevation of the temperature (from 240°C to 260°C) of the molten solder doubles or almost triples the dissolution rate.

Ability of certain solders to dissolve silver or other metals present in TFC has a great impact on leaching. A significant loss of layer thickness may decrease the mechanical integrity of a circuit.

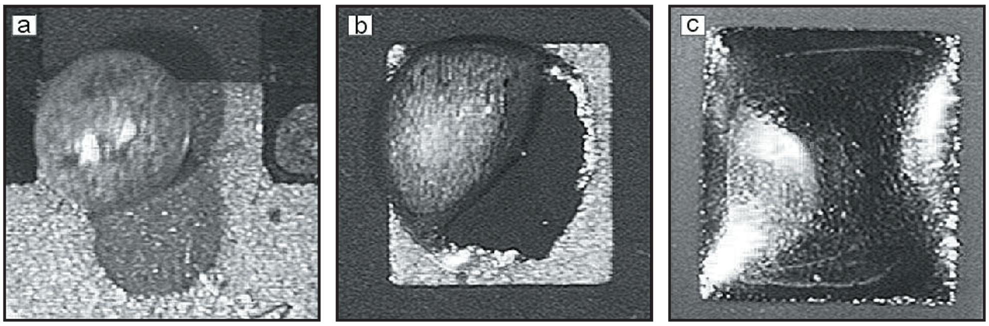
The leach resistance has been evaluated for already mentioned Ag conductors made of pastes coming from three different vendors (A, B and C) [13]. The tests were carried at 240°C, as it was described for 63Sn37Pb solder. The measured value was the time (in seconds) while leaching silver out of layer. Tab. 3 presents the results of those measurements.

Table 3. Time of silver leaching out of the thick film layer by Sn/Pb solder at 240ºC [13].
Tabela 3. Czas wyługowania srebra z warstwy grubej przez Sn/Pb i inne lutowia w temperaturze 240°C [13].

Solder / Layer	63Sn37Pb	96.5Sn3.5Ag	85.2Sn4.1Ag 2.2Bi0.5Cu8In	88.5Sn3Ag 0.5Cu8In
A	<1	6	1	1
B	7	96	52	37
C	>180	>180	>180	>180

Properly composed thick film conductor materials, as it was shown in case of paste C, prove that thick film conductor may still perform a very good leach resistance to the molten solder.

Solder shrinking caused by leaching of silver layers A, B and C is presented in Fig. 6.



1 2 3

Fig. 6. The images of joints after the leaching tests: 1. layer A after 1s; 2. layer B after 7s; 3. layer C after 180s [13].'

Rys. 6. Widok połączeń lutowniczych po teście ługowania: 1. warstwa A po 1s; 2. warstwa B po 7s; 3. warstwa C po 180s [13].

Common way to reduce leaching of Ag from silver bearing thick film conductors is addition of silver to the solder. Dissolution of silver during the soldering, like majority of processes accompanying soldering, is a diffusion controlled process. It is mostly driven by concentration gradient and temperature.

4.2. Intermetallic compounds

Formation of intermetallic compounds is a separate issue. In the past a great deal of research has been done to disclose all the phenomena occurring in the process of soldering thick film conductors with SnPb solders. Those include formation of intermetallic compounds. With the advent of lead-free solders most of the research on intermetallic compounds was focused on copper in PCB. This was not the case with thick film technology. Therefore, it is worthwhile to recall these achievements and compare intermetallic formation phenomenon in TFC.

As it was already mentioned most of thick film conductors are composed with more than one metal. Silver bearing conductors often contain palladium and/or platinum. Same concerns gold conductors. Pd and Pt are added because they are considerably less susceptible to molten solder dissolution. Silver alloyed with Pt and/or Pd is less prone to the electromigration. Metallurgical reactions between solder and thick film material, during the soldering and after the joint solidification are far more complex comparing with the occurrence at the interface solder/copper layer.

The other factor is a new approach to a very important problem of formation of intermetallic compounds. Chemistry of SnAg(Cu) solders does not differ much from chemistry of SnPb(Ag) solder. Lack of lead presence seems to be irrelevant because Pb does not form IMC with the metals contained in the thick film conductors (Ag, Pd, Pt, Au, and Cu). However, the concentration of tin is much higher. It may influence, together with higher soldering temperature, equilibrium and rate of reactions of intermetallic compounds formation.

4.2.1. 63Sn37Pb solder over Pd/Ag thick film conductors

Ag/Pd-based conductors are the most commonly used alloy system in thick film hybrid circuits. One of the main factors that affect reliability of the thick film solder joints is the interaction of the Pd/Ag conductor metallization and SnPb solder. Investigation carried in relation to diffusion of elements, intermetallic compounds formation, and the effects of temperature cycling tests on solder joints adhesion showed that swelling within the conductor layer due to the lager volume of IMCs formed during soldering and service life, decreased the adhesion strength.

Li et al. [15] studied inter-diffusion and IMCs formation between PdAg thick film metallization and 62Sn36Pb2Ag solder. The thick film Pd/Ag layers were prepared in a standard way, and then surface mount passive components were assembled by means of infrared reflow using solder paste 62Sn36Pb2Ag. Test samples were aged isothermally in an oven at 70, 100 and 150ºC for periods of 0, 2, 5, 11, 20, 32, and 47 days. BSE SEM micrographs and X-ray element dot mapping were taken at the interface of the conductor metallization and the solder. Fig. 7 shows BSE SEM micrographs and X-ray mapping of Pb, Sn, Ag and Pd [15]. Ag and Pd mapping demonstrates that a distinct layer of metallization, approximately 10 µm thick, remains next to the ceramic substrate. Aging at 150°C lead to the observation that Sn diffusion into the Pd/Ag layer is evident, and it reaches the conductor/substrate interface after 120 hours of aging. The Ag and Pd mapping reveals that the longer is the aging time the more serious is Ag and Pd diffusion into the solder, with Ag diffusion rate somewhat lower than that of Pd. It is worth noting that silver-rich areas exist in the bulk of the 62Sn36Pb2Ag solder (column 1 and 2). This may be a direct conformation of the presence of Ag_3Sn primary crystals in the bulk solder.

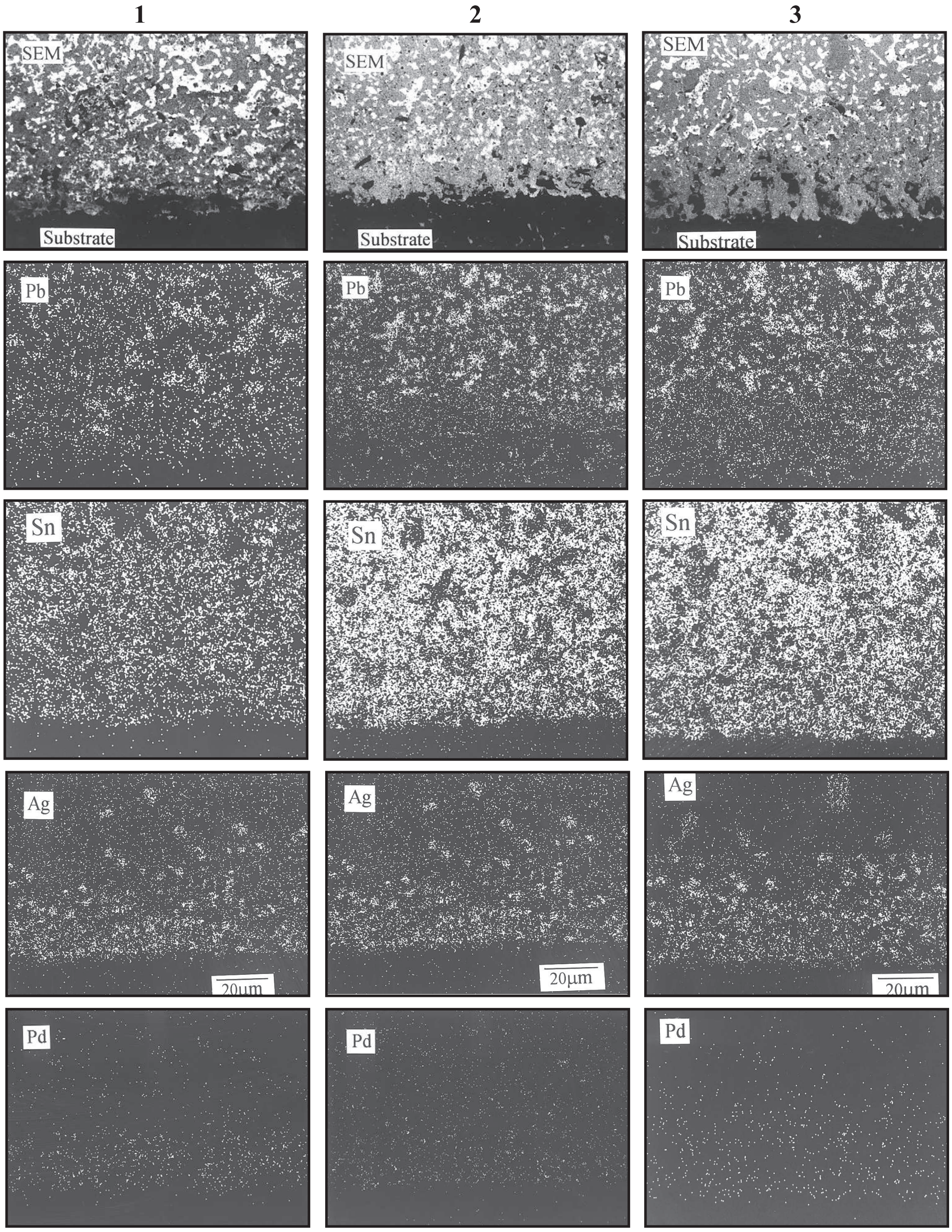


Fig. 7. Backscattered SEM pictures and X-ray elements mapping of cross-section of the solder joints [15]:
column 1 – before aging,
column 2 – after 5 days of aging at 150ºC,
column 3 – after 47 days of aging at 150ºC.

Rys. 7. Obrazy SEM w świetle odbitym i analiza rentgenowska rozkładu pierwiastków przekrojów połączeń lutowniczych [15]:
kolumna 1 – przed starzeniem,
kolumna 2 – po starzeniu w ciągu 5 dni w 150°C,
kolumna 3 – po starzeniu w ciągu 47 dni w 240°C.

The measured depth of the diffusion of silver and palladium in all solder joints enabled the authors [15] to determine relation between the one-dimension diffusion depth and aging time according to the equation (3):

$$d = \sqrt{2D \cdot t} \tag{3}$$

where: d – is diffusion depth,
t – is time,
D – diffusion coefficient.

The plotted relation between mean diffusion depth and square root of aging is shown in Fig. 8 – 9.

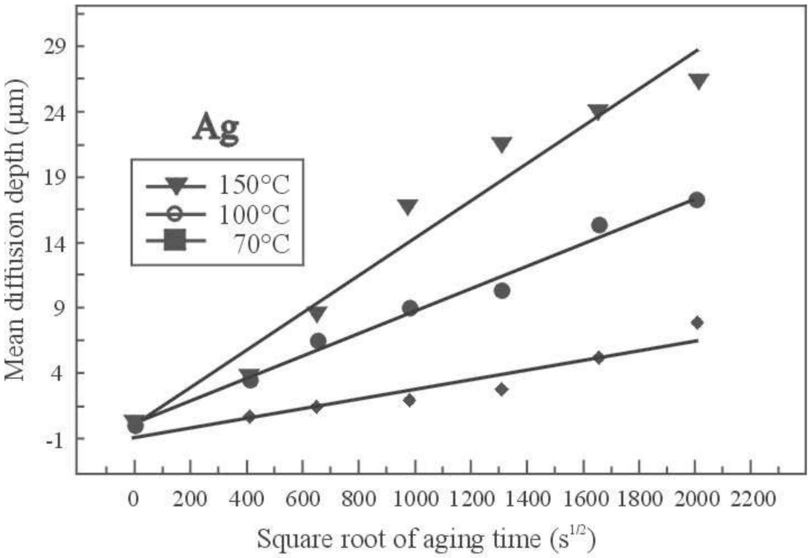


Fig. 8. Diffusion depth of Ag versus square root of aging time for thick film joint aged at 70, 100 and 150ºC [15].
Rys. 8. Głębokość dyfuzji Ag w zależności od pierwiastka kwadratowego czasu starzenia połączenia lutowniczego w temperaturze 70, 100 i 150°C [15].

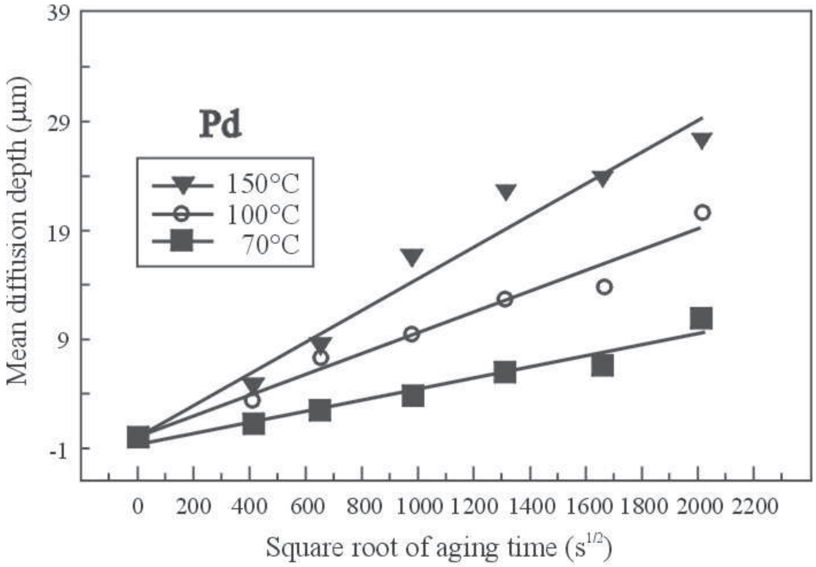


Fig. 9. Diffusion depth of Pd versus square root of aging time for thick film joint aged at 70, 100 and 150ºC [15].

Rys. 9. Głębokość dyfuzji Pd w zależności od pierwiastka kwadratowego czasu starzenia połączenia lutowniczego w temperaturze 70, 100 i 150°C [15].

From the equation (3) and Fig. 8 diffusion rate of Ag has been determined and was found to be 3.01, 7.05, and 14.16 $\mu m/s^{1/2}$, for the aging temperature 70, 100, and 150ºC, respectively.

Pd diffusion rate (Fig. 9) has been found 4.81, 9.63, and 14.45 $\mu m/s^{1/2}$, for the aging temperature 70, 100, and 150ºC, respectively.

The usefulness of these diffusion data were assessed through comparing the measured diffusion rate in surface mounted thick film solder joints in real industrial assemblies aged at room temperature with that calculated using the calculated data. These values are useful in predicting the silver diffusion depth in the thick film solder joints after electronic assembly operated at different thermal conditions for various periods of time and contribution of diffusion depth to their reliability factor. Fig. 10 presents the plots of predicted and real diffusion depth of silver.

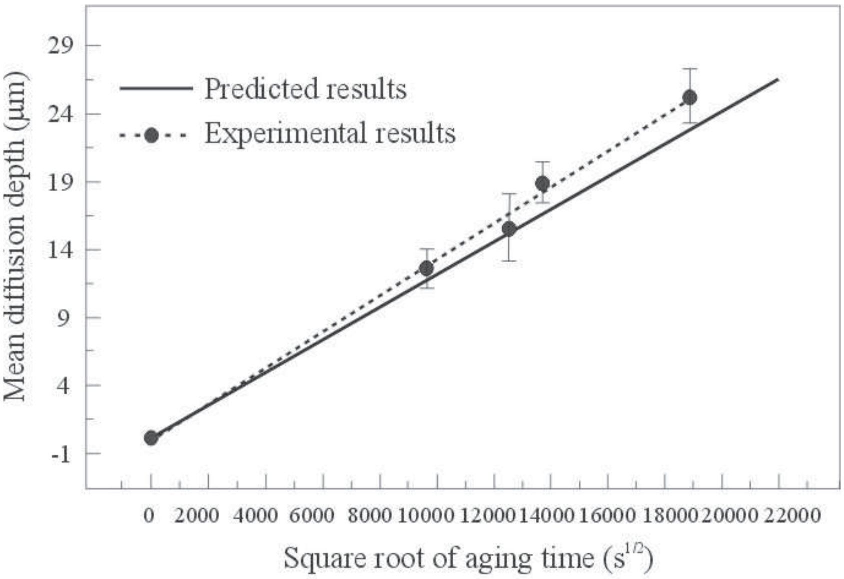


Fig. 10. Predicted and real diffusion depth of silver as a function of square root of aging time.
Rys. 10. Przewidywana i zmierzona głębokość dyfuzji srebra w zależności od pierwiastka kwadratowego czasu starzenia.

According to the results of X-ray diffraction measurements, shown in Fig. 11 several intermetallic compounds Ag_5Sn, Ag_3Sn, Pd_3Sn_2, Pd_2Sn, $PdSn_2$, $PdSn_4$, PdSn, Pd_3Pb, Pd_5Pb_3 coexist in the solder joint of thick film Pd/Ag metallization. The intermetallic compound growth in solder joints is an ordinary diffusional growth and according to the authors [15] should be controlled by interdiffusion of the conductor metallization and the solder elements.

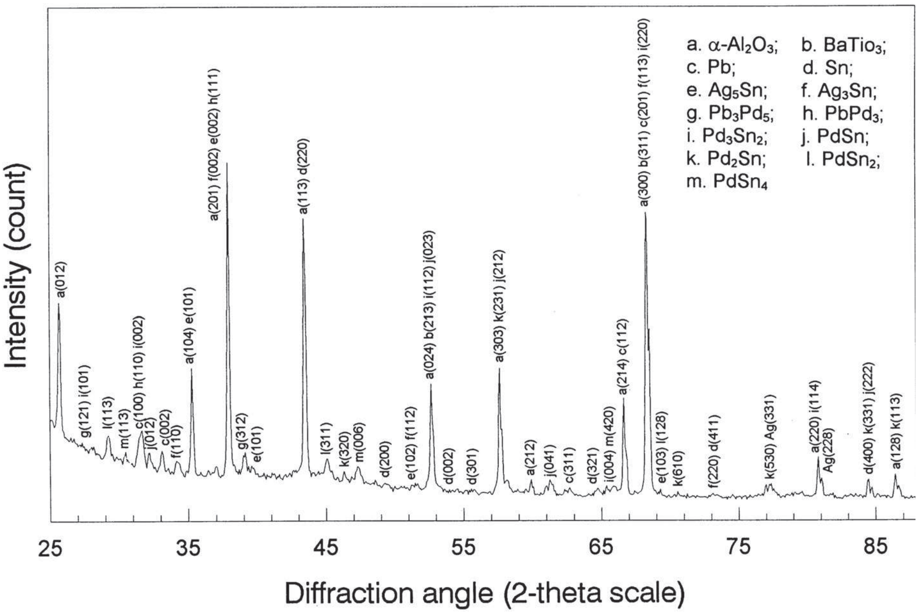


Fig. 11. X-ray diffraction pattern of a cross-section of a solder joint, after 47 days of aging at 100ºC [15].

Rys. 11. Dyfrakcyjna analiza rentgenowska przekroju połączenia lutowniczego po 47 dniach starzenia w 100°C [15].

4.2.2. Sn and Sn3.5Ag solder over Ag thick film conductors

The use of silver in thick film materials has been a long lasting tradition. Being relatively inexpensive, comparing with other noble metals such as Au, Pd and Pt, silver was very much wanted as a universal component of conductive pastes. Unfortunately, several weaknesses, e.g. ion migration under humid condition or poor resistance to solder leaching, exhibit by silver did not allow exploiting it in high reliability appliance (multilayer structures, military and space devices, etc.). Improvement of silver properties by using silver alloys with platinum or palladium is rather costly. Addition of 1% of platinum doubles or even triples the cost of metals included to the paste (depending on the actual price of Pt).

Things has changed after half a century of very intense research of many laboratories at research institutes or carried by pastes manufacturers on extending of pure silver application (without addition of the costly noble metals). Now-a-days silver pastes are very important thick film material, which can be used in multilayer structures or in LTCC technology. Latest works on getting rid of "ceramic lead" contained in thick film circuits had beneficial influence on present properties of silver paste.

No surprise, that the effect of soldering of silver conductors was a major concern of researchers dealing with thick film materials and/or solders.

Su et al. [16] investigated interfacial reactions of liquid Sn and Sn3.5Ag solders with silver thick films. Their main concern was to study the liquid/solid inter-diffusion. To solder silver thick film layers of 10 μm thickness, foils of Sn and Sn3.5Ag 0.2 mm thick were used. On the Ag/alumina substrate the foil (same size as the Ag pad) was placed, and heated to the temperatures 250-325ºC, under vacuum (10^{-3} torr) in an IR oven. Soldering process was aided by a flux. The cross-sections of Ag layers soldered under various conditions were examined by SEM. Fig. 12 shows SEM pictures of the cross-section of Ag layer reacted with Sn.

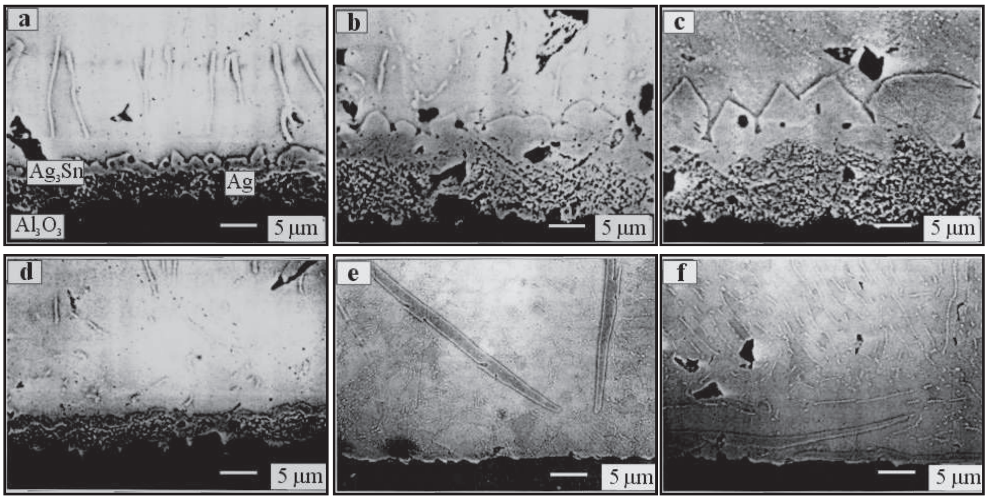


Fig. 12. Micrographs of the interfacial intermetallic compounds and matrix precipitates formed during soldering reaction between liquid Sn and the Ag thick film [16]:
(a) 250ºC, 20 minutes, (b) 250ºC, 25 minutes, (c) 250ºC, 30 minutes,
(d) 300ºC, 7 minutes, (e) 300ºC, 15 minutes, (f) 300ºC, 18 minutes.

Rys. 12. Zdjęcia mikroskopowe związków międzymetalicznych na granicy faz i matryca wytrąceń powstałych w czasie reakcji lutowania, pomiędzy stopionym Sn a Ag zawartym w warstwie [16]:
(a) 250°C, 20 minut, (b) 250°C, 25 minut, (c) 250°C, 30 minut,
(d) 300°C, 7 minut, (e) 300°C, 15 minut, (f) 300°C, 18 minut.

The electron probe microanalysis (EPMA) and x-ray diffractometry (XRD) revealed that Ag_3Sn phase is the relevant IMC.

Fig. 12 illustrates that Ag diffuses from the thick film into the pure Sn matrix for a distance of about 13 μm, after soldering reaction at 250ºC for 20 minutes. The needle-type precipitate is observed near the Ag/Sn interface, which is the Ag_3Sn phase as analyzed by EPMA. The Ag_3Sn phase is not seen in the main body of the Sn matrix. Longer period of soldering and/or elevating temperature of soldering make that Ag_3Sn IMC appears in the entire Sn matrix. Fig. 12b–d, show that the residual Ag thick film becomes porous after soldering reaction. This correlates with a heavy diffusion of Ag from the sintered conductor into the Sn matrix. The final stage of silver consumption process is seen in Fig. 12e–12f when certain amount of IMC is settled at the Sn/Al_2O_3 interface.

The morphology of the interfacial IMCs formed during the soldering reaction between Sn3.5Ag solder and Ag thick film, shown in Figure 13, is similar to that describe above. However, the Ag_3Sn phase can be found in the entire solder volume, even at early stage of soldering (Fig. 13a), what means that the IMC is originated from Ag present in the solder. In this case, the residual layer is thicker. At the final stage of reaction of Sn3.5Ag solder with the Ag thick film, the floating of large intermetallic bands is observed (Fig. 13e –13f). Fig. 13e gives a strong indication that such floating intermetallic bands have been stripped from the solder/substrate interface.

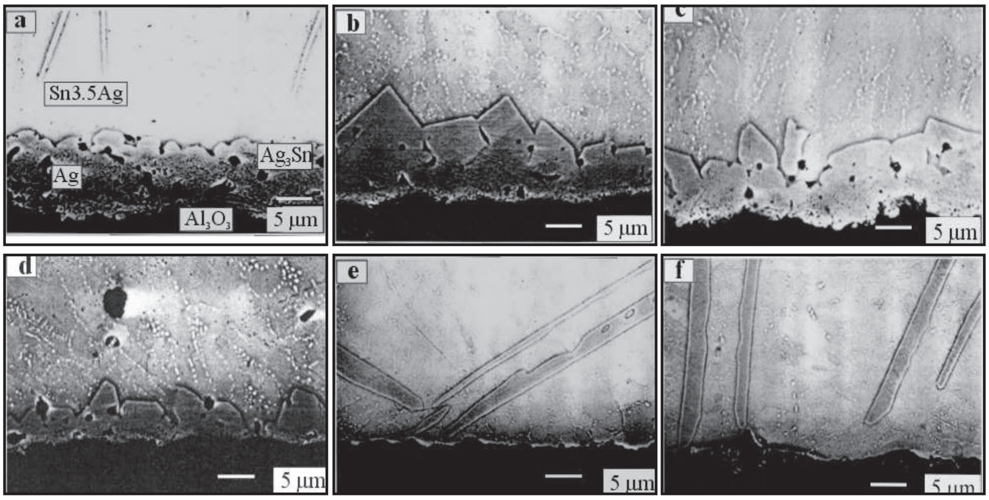


Fig. 13. Micrographs of the interfacial intermetallic compounds and matrix precipitates formed during soldering reaction between liquid Sn3.5Ag and the Ag thick film:
(a) 250ºC, 20 minutes, (b) 250ºC, 28 minutes, (c) 250ºC, 32 minutes,
(d) 300ºC, 12 minutes, (e) 300ºC, 16 minutes, (f) 300ºC, 20 minutes [16].

Rys. 13. Zdjęcia mikroskopowe związków międzymetalicznych na granicy faz i matryca wytrąceń powstałych w czasie reakcji lutowania, pomiędzy stopionym Sn3.5Ag a Ag zawartym w warstwie [16]:
(a) 250°C, 20 minut, (b) 250°C, 28 minut, (c) 250°C, 32 minut,
(d) 300°C, 12 minut, (e) 300°C, 16 minut, (f) 300°C, 20 minut.

The dissolved thickness (X_D) of the Ag thick film was estimated as follows:

$$X_D = X_1 - X_R - X_{IM}^{Ag} = X_1 - X_R - (3/4)X_{IM} \tag{4}$$

where:
X_I is the initial thickness of Ag thick film,
X_R is the residual thickness of the Ag thick film,
X_{IM} is the thickness of the interfacial IMC,
X_{IM}^{Ag} is the partial thickness of Ag in the IMC.

The thicknesses of the interfacial intermetallic compounds (X_{IM}) formed during the soldering reactions of Sn and Sn3.5Ag with silver thick films under various conditions are summarized in Tab. 4–5.

Table 4. Thickness of the interfacial intermetallic compounds after soldering reaction between liquid Sn and Ag thick film [16].
Tabela 4. Grubość związków międzymetalicznych na granicy faz powstałych w czasie reakcji lutowania, pomiędzy stopionym Sn a Ag zawartym w warstwie [16].

T, ºC	t, min	X_{IM}, µm	X_R, µm	X_{IM}^{Ag}, µm	X_D, µm
250	20	2.2	4.8	1.7	3.5
250	25	4.8	4.1	3.6	2.3
250	30	6.6	3.2	5.0	1.8
275	9	2.3	3.2	1.7	5.0
275	15	5.4	2.8	4.0	3.2
275	20	7.0	1.0	5.2	3.4
300	7	1.6	3.2	1.2	5.6
325	5	2.8	1.6	2.1	6.4

Table 5. Thickness of the interfacial intermetallic compounds after soldering reaction between liquid Sn3.5Ag and Ag thick film [16].
Tabela 5. Grubość związków międzymetalicznych na granicy faz powstałych w czasie reakcji lutowania, pomiędzy stopionym Sn3.5Ag a Ag zawartym w warstwie [16].

T, ºC	t, min	X_{IM}, µm	X_R, µm	X_{IM}^{Ag}, µm	X_D, µm
250	20	2.4	7.9	1.3	0.2
250	28	4.6	5.7	3.4	0.8
250	32	5.6	5.6	4.2	0.3
275	20	2.5	6.3	1.9	1.8
275	24	4.7	5.7	3.5	0.8
275	28	5.5	5.3	4.2	0.6
300	12	4.8	5.7	3.6	0.7

The plotted relations of the thicknesses of the interfacial IMC (X_{IM}) versus the reaction time are shown in Fig. 14. The linearity of these relations indicates that the growth of interfacial IMC during reactions of Sn or Sn3.5Ag solders with silver thick films are interface-controlled.

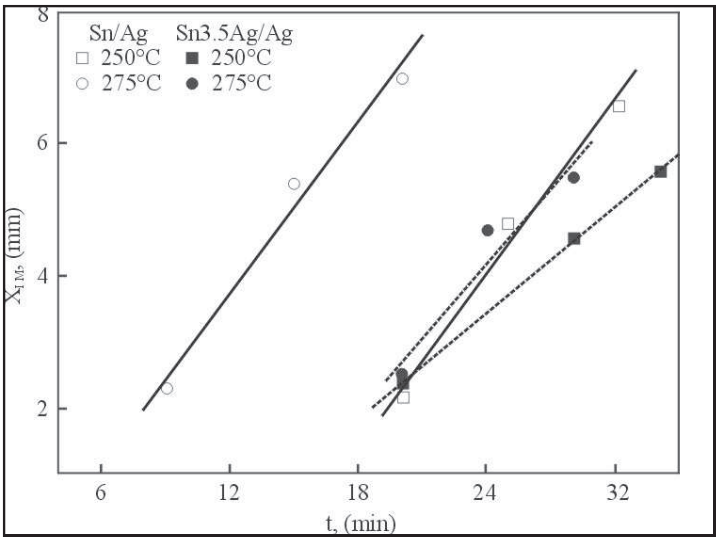


Fig. 14. The thickness of interfacial IMC (X_{IM}) formed during soldering reaction of liquid Sn or Sn3.5Ag with Ag film versus the reaction time (t) [16].

Rys. 14. Grubość związków międzymetalicznych (X_{IM}) na granicy faz powstałych w czasie reakcji lutowania, pomiędzy stopionym Sn lub Sn3.5Ag a Ag zawartym w warstwie w zależności od czasu reakcji (t) [16].

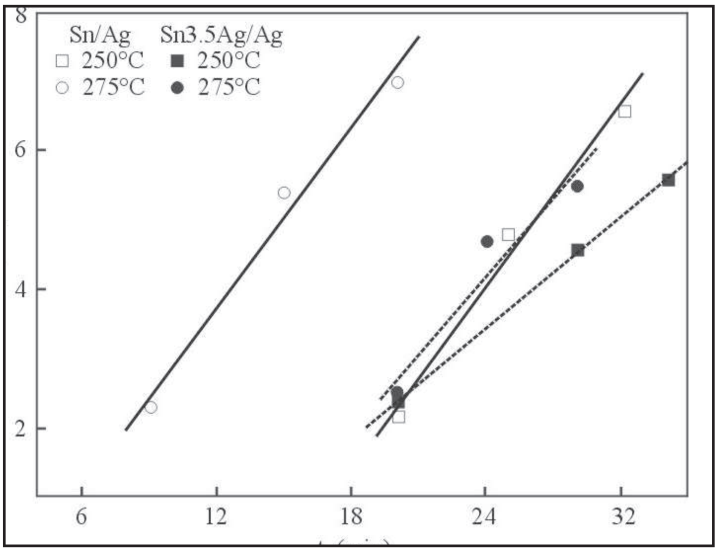


Fig. 15. Calculated thickness (X_C) of consumed Ag after soldering reaction of liquid Sn (or Sn3.5Ag) with Ag thick films versus the reaction time (t) [16].

Rys. 15. Obliczona grubość (X_C) przereagowanego Ag po reakcji Sn (lub Sn3.5Ag) z Ag zawartym w warstwie w zależności od czasu reakcji (t) [16].

Fig. 15 presents the plots of silver consumption during the soldering reaction, which appears to be also governed by a linear reaction. The consumed thickness (X_C) of the Ag thick film was calculated from the equation (5):

$$X_C = X_I - X_R \quad (5)$$

where:

X_I – is the initial thickness of the Ag layer,
X_R – is the residual thickness of the Ag layer.

The soldering reactions of Sn or Sn3.5Ag with silver thick films produce scallop-shaped Ag_3Sn IMC at the solder/silver layer interface. Needle-like precipitates are formed in the solder matrix and then transformed into fine particles. At the final stage of soldering reactions, a number of large Ag_3Sn intermetallic bands can be observed. Kinetic analysis shows that the growth of interfacial IMC during the Sn/Ag or Sn3.5Ag/Ag soldering reactions are interface-controlled and the growth rates are similar in both cases. The appearance of precipitates in Sn matrix gives the evidence of the silver dissolution in the molten Sn, as well as in the molten Sn3.5Ag solder. The dissolution rate of Ag during the reaction of pure tin with silver thick film layer is about four times higher than that during the reaction with Sn3.5Ag alloy.

4.2.3. In49Sn solder over Ag thick film conductors

It is believed that lowering the temperature of soldering may reduce harmful impact on the solder/thick film joints. Indium could be a very useful alloying metal to lower the melting temperature of solders. Chuang et al. [17] compared the interfacial reactions of In49Sn eutectic with Ag thick film and Ag plated layer. From their previous work they new that a scallop-shaped Ag_2In phase enveloped in an $AgIn_2$ thin outer layer was appearing at the interface liquid solder/plated Ag. The growth kinetics of Ag_2In followed the parabolic law and was diffusion controlled. Unfortunately, the authors carried their experiments with extremely thick silver layer - 70±2 μm, as for silver thick films which normally fall into 10 to 20 μm interval. Nevertheless, they came to very interesting and important conclusions. In contrast to findings regarding the kinetics of IMC growth at the interface In49Sn alloy/silver plated substrates (or copper PCB), the kinetics of IMC growth at the interface In49Sn alloy/thick film silver does not follow the parabolic low. Kinetics of the reaction of In49Sn solder with silver thick film exhibits linear growth of the Ag_2Sn intermetallic compound. Such linear growth of IMC during the soldering reaction between In49Sn and the Ag thick film is attributed to the porosity of the sintered Ag thick film. As the liquid solder penetrates into the porous layer the reaction conditions change rapidly, influencing the reaction kinetics.

4.2.4. SnBi(Cu) solders over Cu and PtAg thick film conductors

Miao et al. [18] studied aging effects of solder joints produced by soldering Cu and Pt/Ag thick films with 42.4Sn57.6Bi nearly eutectic binary alloy or 41.6Sn57.4Bi1.0Cu ternary alloy. Simultaneously, soldered copper on FR4 substrates was examined for comparison. Thick film (TF) samples were aged at 120ºC and PBC – at 100ºC, for 100 days. Meanwhile, the microstructure, morphology of solder/conductor and phase identification was carried. The authors came to the following conclusions.

A single IMC Cu_6Sn_5 is observer in the eutectic SnBi/Cu-FR4 joint after aging at 100ºC.

Significant coarsening of Bi-rich phase is observed in the binary eutectic SnBi joint. Addition of 1% Cu into the binary alloy substantially reduces that coarsening. Identical trend is exhibited in the solder joint with both Cu and Pt/Ag thick films on alumina substrate.

In both SnBi/Cu-TF and SnBi1.0Cu/Cu-TF joints, Cu_6Sn_5 IMC is formed after aging at 120ºC. Ag_3Sn IMC is observed in both SnBi/PtAg-TF and SnBi1.0Cu/PtAg-TF joints.

The formation of Ag_3Sn IMC in the SnBi1.0Cu solder with PtAg thick film is planar.

The formation of Cu_6Sn_5 IMC in the SnBi1.0Cu solder with Cu thick film is scallop-like.

The growth of Ag_3Sn IMC is diffusion controlled. The thickness of Ag_3Sn IMC is reduced in the ternary SnBi1.0Cu/PtAg-TM joint as compared to that in the binary eutectic SnBi/PtAg-TF joint.

4.2.5. SnAgBi(Au) solders over Au/Pt/Pd thick film conductors

Very high reliability applications such as aircraft avionics and military hardware require materials resistant to harsh, humid and/or oxidizing environment. Under such circumstances silver conductors must be replaced by more reliant metal, namely gold. Gold conductors are very useful in applications where terminations are created by means of wire bonding. Standard soldering of gold conductors is almost impossible, since it dissolves very rapidly in molten Sn-base solders. The use of AuPt, AuPd or Au/Pt/Pd alloys is the way to produce conducting thick film layers, which are solderable as well as wire-bondable.

Vianco et al. [19] and Vianco [20] carried detailed study on intermetallic compounds growth of lead-containing (63Sn37Pb) [19] and lead-free (91.84Sn3.33Ag4.83Bi and 86.85Sn3.15Ag5.0Bi-5.0Au) [20] solders at the interface with thick film conductor having metal composition 76Au21Pt3Pd, printed on alumina substrate. The double printed conductor layers were of nominal thickness 20 μm. The solder pastes printed through the stencil 1:1 were reflowed in a nitrogen oven at 260ºC, using profile described in [21].

The solid state aging was carried at 55ºC, 70ºC, 85ºC, 100ºC, 135ºC or 170ºC. The periods of aging time ranged from 10 to 5000 hours. Vianco [20] adopted well describe method of measuring the thickness of the IMC making use of the SEM(BSE) images of solder/thick film interface. The IMC thickness data were used to determine the rate of kinetics of the growth process. The values of kinetics parameters A, n and ΔH were determined by performing a multivariable regression analysis using the equation (6) [19]:

$$\ln(x - x_0) = \ln A + n \ln(t) - \frac{\Delta H}{RT} \tag{6}$$

where: x (m) = layer thickness at time t (s),
x_o(m) = initial thickness at t = 0,
n = time exponent,
ΔH (kJ/mol) = apparent activation energy,
R = universal gas constant, (8.314 J/mol∗K),
T (K) = absolute temperature.

Vianco [20] made an interesting observation noticed also from their previous work [19]. The IMC layer thickness measured following aging treatment at low temperatures (55ºC and 70ºC) were less than that measured for the as fabricated. The hypothetical explanation is that the equilibrium state just after solidification, was in fact metastable relative to the equilibrium state that would prevail at room temperature. The latter equilibrium preferred a thinner IMC layer – $x_o = 1.77$ µm. Under the slightly accelerated kinetics the IMC layer thickness decreased to accommodate the low-temperature equilibrium. The drop in layer thickness presented certain complication which was neatly over-came by the author.

Plots of the logarithm of IMC layer growth, $\ln(x-x_o)$ as a function of logarithm of time ln(t), were split into two groups because of a different characteristic of the plots. The IMC layers aged at low temperature (55ºC, 70ºC) were showing low increase of layer thickness due to contraction of the IMC layer and simultaneous growth of the IMC layer as a response to the accelerated aging condition (Fig. 16a). The main feature of the plots of high-temperature aging (135ºC and 170ºC) is that the incubation period can be hardly observed, and that the IMC layer growth reached a plateau (Fig. 16b). Further thickness increases were no longer observed. The plot related to aging at 85ºC was somewhere in between the two series, and aged at 100ºC – rather closer to the high-temperature aging series.

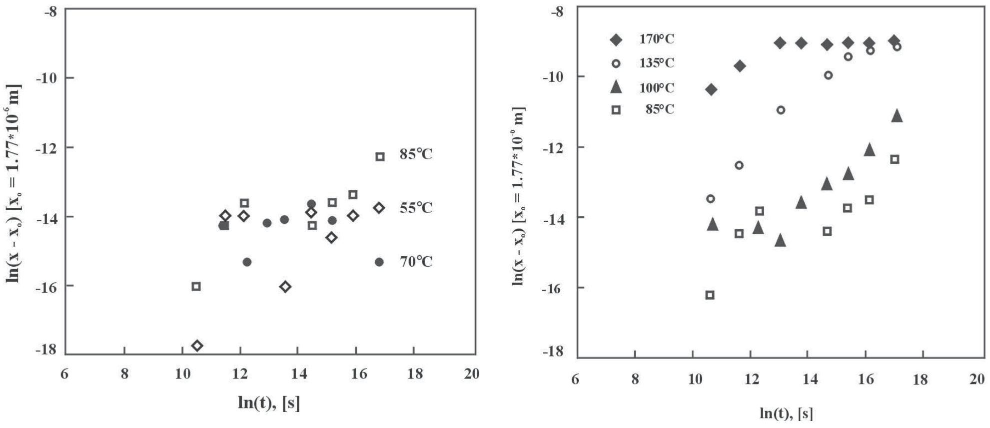


Fig. 16. Plot of ln of IMC layer thickness growth versus ln(t) – SnAgBi/AuPtPd soldering:
(a) low-temperature aging - 55ºC, 70ºC, 85ºC (left),
(b) high-temperature aging - 85ºC, 100ºC, 135ºC or 170ºC (right) [20].

Rys. 16. Wzrost grubości warstwy związków międzymetalicznych w zależności od czasu starzenia w różnych temperaturach – w układzie logarytmicznym, dla złącza SnAgBi(lutowie)/AuPtPd(warstwa):
(a) starzenie niskotemperaturowe – 55°C, 70°C, 85°C (po lewej),
(b) starzenie wysokotemperaturowe – 85°C, 100°C, 155°C i 170°C (po prawej) [20].

Courtesy of IMAPS - International Microelectronics and Packaging Society

The same procedure was applied to an experiment where the behavior of the other solder 86.85Sn3.15Ag5.0Bi-5.0Au on top of Au/Pt/Pd thick film was studied. The similarity of plots obtained for low-temperature aging, as well as high-temperature aging, with those obtained for the previous solder (SnAgBi) is shown in Fig. 17 (a–b).

Worth noticing are some differences: the IMC layer thickness as-fabricated was 1.3±0.3 µm that is significantly thinner than that for the SnAgBi solder (Fig. 18 – top-right), and extent of infiltration into and dissolution of the thick film layer was smaller in case of the SnAgBiAu solder.

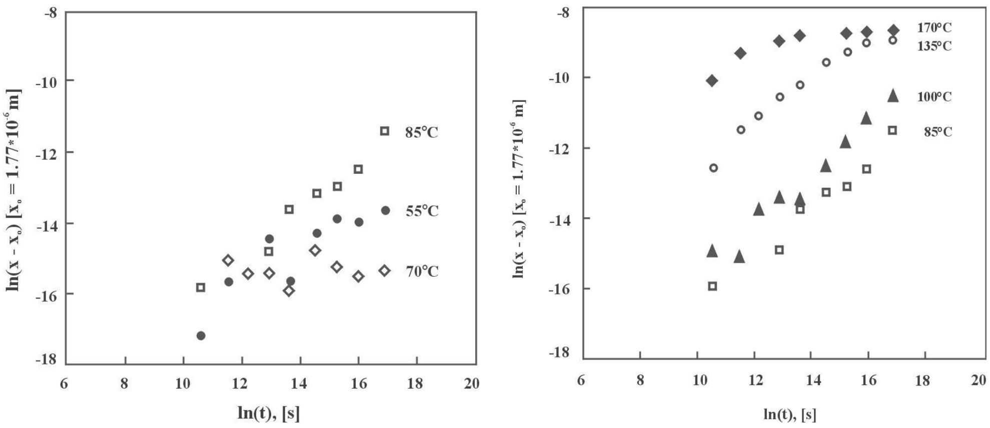


Fig. 17. Plot of ln of IMC layer thickness growth versus ln(t) – SnAgBiAu/AuPtPd soldering:

(a) low-temperature aging - 55ºC, 70ºC, 85ºC (left),

(b) high-temperature aging - 85ºC, 100ºC, 135ºC or 170ºC (right) [20].

Rys.17. Wzrost grubości warstwy związków międzymetalicznych w zależności od czasu starzenia w różnych temperaturach – w układzie logarytmicznym, dla złącza SnAgBiAu(lutowie)/AuPtPd(warstwa):

(a) starzenie niskotemperaturowe – 55°C, 70°C, 85°C (po lewej),

(b) starzenie wysokotemperaturowe – 85°C, 100°C, 155°C i 170°C (po prawej) [20].

Courtesy of IMAPS - International Microelectronics and Packaging Society

Top-left picture presents SEM/BSE image of a cross section of SnAgBi/AuPtPd as fabricated. The IMC thickness was already 3.4±0.2 μm, with $AuSn_4$ needle-like particles dispersed in the solder field as a result of dissolution of thick film by the molten solder during the wetting-and-spreading process. A heavy infiltration of the solder into the pores (channels) of thick film is visible.

The bottom raw clearly indicates the complete consumption of the thick film after 5000 hour aging at 135ºC. The overall appearance of microstructure looks much similar in case of solders. The exceptional is the relatively ragged interface formed between the SnAgBiAu solder and the intermetallic compound.

Electron microprobe analysis (EMPS) revealed that the IMC of aged joints made of both solders exhibited a stoichiometry of (Au, Pt, Pd)Sn_4, with Au 70%, Pt 20% and Pd 10% percentage, that is corresponding to the thick film composition. However, at early stage of aging the joints of SnAgBiAu solder the IMC layer was almost solely of Au and Sn. The longer time of aging caused an increase in Pt and Pd levels to values that were nearly identical to those observed in the IMC layer formed with SnAgBi solder. The faster growth the IMC layer (thick ragged interface) with the SnAgBiAu solder was caused by the physical incorporation $AuSn_4$ particles from the solder matrix.

Fig. 18 illustrates the progress of aging.

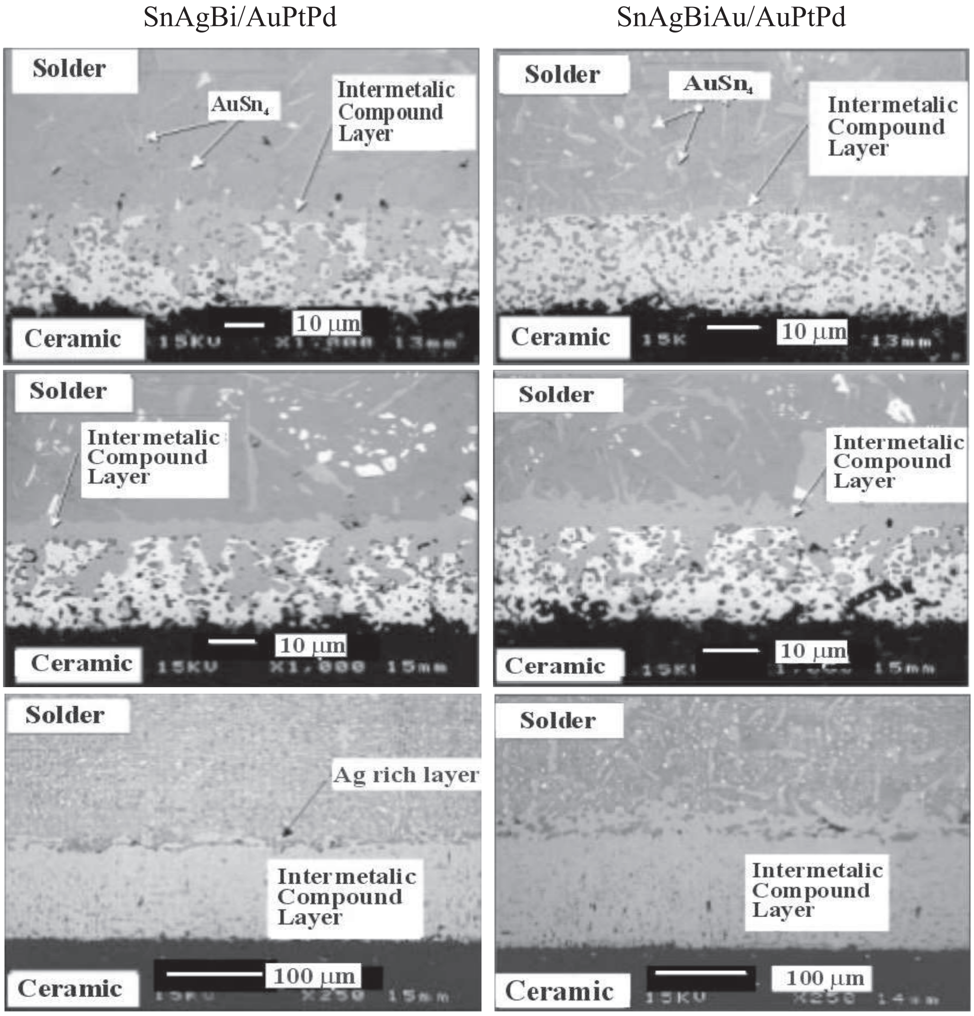


Fig. 18. SEM/BSE micrograph showing a cross section of:

1. the SnAgBi solder bump on Au/Pt/Pd thick film (left column),
2. the SnAgBiAu solder bump on Au/PtPd thick film (right column):
   a. as-fabricated (top raw),
   b. aged at 100ºC for 1000 hours (middle raw),
   c. aged at 135ºC for 5000 hours (bottom raw) [20].

Rys. 18. Zdjęcia SEM/BSE przekrojów:

1. wypustka (bump) lutowia SnAgBi na warstwie Au/Pt/Pd (kolumna lewa),
2. wypustka (bump) lutowia SnAgBiAu na warstwie Au/Pt/Pd (kolumna prawa):

a. bezpośrednio po wytworzeniu (rząd górny),
b. po starzeniu w 100ºC przez 1000 godzin (środkowy rząd),
c. po starzeniu przez 135ºC przez 5000 (dolny rząd). [20].

Courtesy of IMAPS - International Microelectronics and Packaging Society

After removing the IMC growth data that were impacted by either incubation phenomena or the thick film consumption, the obtained data were used to calculate the rate of the reaction. The multivariable regression analysis resulted in the values shown in Tab. 6.

Table 6. Results of multivariable analysis of the data obtained in relation to the intermetallic compound layer growth [19–20].
Tabela 6. Wyniki analizy wielofunkcyjnej danych uzyskanych na podstawie wzrostu warstwy związku międzymetalicznego [19–20].

Courtesy of IMAPS - International Microelectronics and Packaging Society

	91.84Sn3.33 Ag4.83Bi	86.85Sn3.15 Ag5.0Bi5.0Au	63Sn37Pb
Pre-exponential term, A	16252	727	13400
Time exponent, n	0.74±0.8	0.63±0.8	0.78±0.8
Apparent activation energy, ΔH, kJ/mol	103±7	87±6	106±8
Solidus temperature, ºC	212	195	183

The values of A, n and ΔH are significantly smaller for 91.84Sn3.33Ag4.83Bi solder. The same values of 63Sn37Pb solder are shown for comparison.

The comparison of SnAgBi and SnAgBiAu solder behavior led to the conclusion that addition of Au to the SnAgBi alloy affects both the growth kinetics and mechanism of formation of the intermetallic compound layer. The author [20], after some computation, made certain prediction regarding aging curves, which were plotted separately for low-temperature (55ºC, 70ºC, and 85ºC) and high-temperature (85ºC, 100ºC, 135ºC, and 170ºC). The plots are shown in Fig. 19–20. The symbols were used to trace the particular temperature results, which do not represent actual experimental data. The trend is contrary to the expected results, since the predicted thickness of the IMC layer was greater for the SnAgBiAu alloy that it was for the ternary alloy SnAgBi. One of the possible explanations is that Au contained in the solder had also contributed to the IMC layer growth.

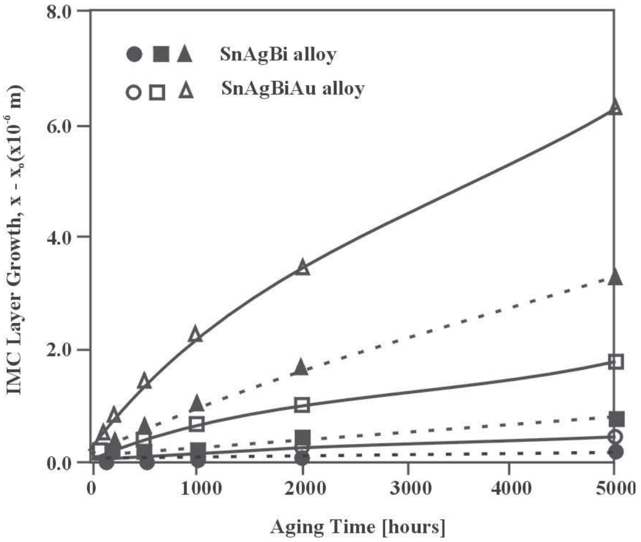


Fig. 19. The predicted IMC layer growth ($x - x_o$), as a function of time for the low-temperature regime (55ºC, 70ºC, and 85ºC).

Rys. 19. Przewidywany wzrost warstw związków międzymetalicznych ($x - x_o$) w zależności od czasu starzenia w reżimie niskotemperaturowym (55ºC, 70ºC i 85ºC).

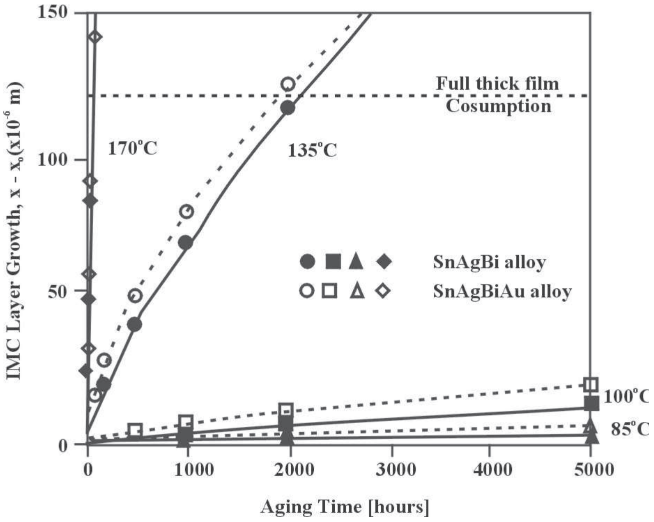


Fig. 20. The predicted IMC layer growth ($x - x_o$), as function of time for the high-temperature regime (85ºC, 100ºC, 135ºC, and 170ºC).

Rys. 20. Przewidywany wzrost warstw związków międzymetalicznych ($x - x_o$) w zależności od czasu starzenia w reżymie wysokotemperaturowym (85ºC, 100ºC, 155ºC i 170ºC).

4.5. Properties of lead-free solder joints on top of thick films

The previous paragraphs were dealing with research aimed at the phenomena occurring during the process of soldering. Another approach, perhaps even more interesting to manufacturers, is evaluating the quality of the ready solder joint. One of the most important properties of a solder joint is adhesion. If the integrity of the joint fails the circuit loses mechanical integrity, and is electrically and thermally disconnected.

Bocalo et al. [23] evaluated lead-free conductive thick film materials using lead free solder alloys. They have selected following solder alloys: Sn3.5Ag, Sn5Ag and Sn4Ag0.5Cu, and thick film materials from Hereaus Inc.: C8727 (Ag), C8729 (Ag), C4727 (AgPt 99:1), 8282 (AgPt 99:1), 8211 (AgPd (8:1) and 8241 (AgPdPt). The pastes were printed onto ceramic substrate, dried and firing at peak temperature 850ºC. The coupons were dipped in the flux and then immersed in the molten solder alloy. Solder acceptance, leach resistance and adhesion have been measure.

The results of solder acceptance and leach resistance are listed in Tab. 7–8.

Table 7. Solder acceptance of lead free conductors using lead free alloys.
Tabela 7. Podatność na lutowanie bezołowiowych warstw przewodzących stopami wolnymi od ołowiu.

Courtesy of IMAPS - International Microelectronics and Packaging Society

Conductor → Solder ↓	C8727 (Ag)	C8729 (Ag)	C4727 (AgPt)	8282 (AgPt)	8211 (AgPd)	8241 (AgPtPd)
Sn5Ag	>95%	>95%	>95%	>95%	>95%	>95%
Sn3.5Ag	>90%	>90%	>95%	>95%	>95%	>90%
Sn4Ag0.5Cu	>95%	>95%	>95%	>95%	>95%	>95%

Table 8. Leach resistance expressed as % loss (total are) of an 80x80 mil pad after multiple 10-seconds dips.
Tabela 8. Odporność na ługowanie lutowiem wyrażona w % zaniku zwilżania pól lutowniczych (2x2 mm) po wielokrotnym, 10-sekundowym zanurzeniu w lutowiu.
Courtesy of IMAPS - International Microelectronics and Packaging Society

	C8727 Ag			C8729 Ag			C4727 AgPt			8282 AgPt			8211 AgPd			8241 AgPtPd		
No. dips	5Ag	3.5Ag	4Ag0.5Cu	5Ag	3.5Ag	4Ag0.5Cu	5Ag	3.5Ag	4Ag0.5Cu	5Ag	3.5Ag	4Ag0.5Cu	5Ag	3.5Ag	4Ag0.5Cu	5Ag	3.5Ag	4Ag0.5Cu
1	5	5	5	5	5	5	5	6	5	5	8	5	5	8	5	5	5	9
2	5	12	5	10	12	11	8	10	5	5	10	7	5	10	8	5	10	9
3	11	18	10	10	19	12	10	14	10	11	15	12	8	12	10	6	13	10
4	14		13	13		14	13		13	13		15	10		14	8		15
5	18		15	20		22	18		19	20		16	22		19	14		17

All adhesion results, presented in Fig. 21-23, are based on a minimum of 30 pulls. All solders alloys were tested at temperatures 20-30ºC above their respective liquidus temperature.

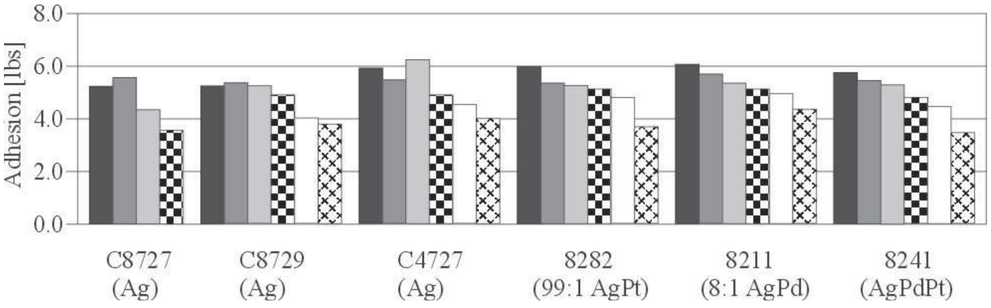
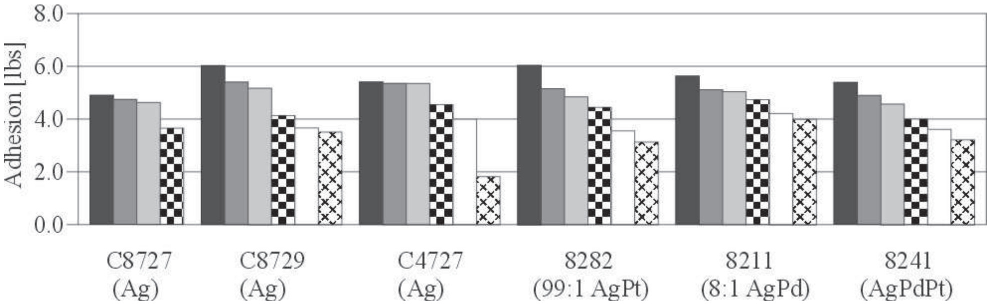


Fig. 21. Aged adhesion at 150ºC of various silver containing conductors tested with Sn3.5Ag solder alloys (the above applies to Fig. 22–23).
Rys. 21. Adhezja po starzeniu w 150ºC różnych warstw zawierających srebro badanych stopem lutowniczym Sn3.5Ag (powyższe odnosi się również do Rys. 22–23).

■ - initial adhesion (adhezja początkowa),
▩ - after 48 hours of aging (adhezja po 48 godz. starzenia),
▒ - after 144 hours of aging (adhezja po 144 godz. starzenia),
▚ - after 250 hours of aging (adhezja po 250 godz. starzenia),
□ - after 500 hours of aging (adhezja po 500 godz. starzenia),
⊠ - after 1000 hours of aging (adhezja po 1000 godz. starzenia).



Courtesy of IMAPS - International Microelectronics and Packaging Society

Fig. 22. Aged adhesion at 150ºC of various silver containing conductors tested with Sn5Ag solder alloys.
Rys. 22. Adhezja po starzeniu w 150ºC różnych warstw zawierających srebro badanych stopem lutowniczym Sn5Ag.

Courtesy of IMAPS - International Microelectronics and Packaging Society.

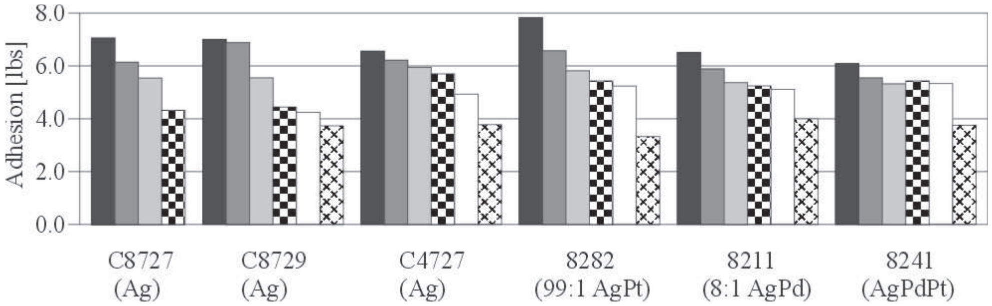


Fig. 23. Aged adhesion at 150ºC of various silver containing conductors tested with Sn4Ag0.5Cu solder alloys.
Fig. 23. Adhezja po starzeniu w 150ºC różnych warstw zawierających srebro badanych stopem lutowniczym Sn4Ag0.5Cu.

Courtesy of IMAPS - International Microelectronics and Packaging Society

All combinations of Ag bearing metallization with solder of high content of Ag (Sn5Ag alloy) performed best in respect of solder leaching. The results of measurements of adhesion and solder acceptance were comparable regardless of the used alloy. The author's [23] recommendation for thick film manufacturers is solder alloy Sn5Ag (first choice) and solder alloy Sn4Ag0.5Cu (second choice).

Achmatowicz et al. [24] conducted similar research as presented above. Comparison of newly elaborated lead free Ag bearing thick film materials with commercial one, as well as their solderability with SnPbAg and Pb-free solder have been made. Standard procedure was used to make thick film samples on alumina substrates. The soldering was carried with the use of commercial solder pastes lead-free (and lead containing for comparison) of the following metallurgy: Sn3.8Ag0.7Cu, Sn3.5Ag and Sn36PbAg2.

The solder acceptance for all samples was evaluated being above 95%. The shear force necessary to separate the mounted 1206 component was the measure of adhesion (initial and after 48 hours aging at 150ºC). The results are presented in Figs. 24-26.

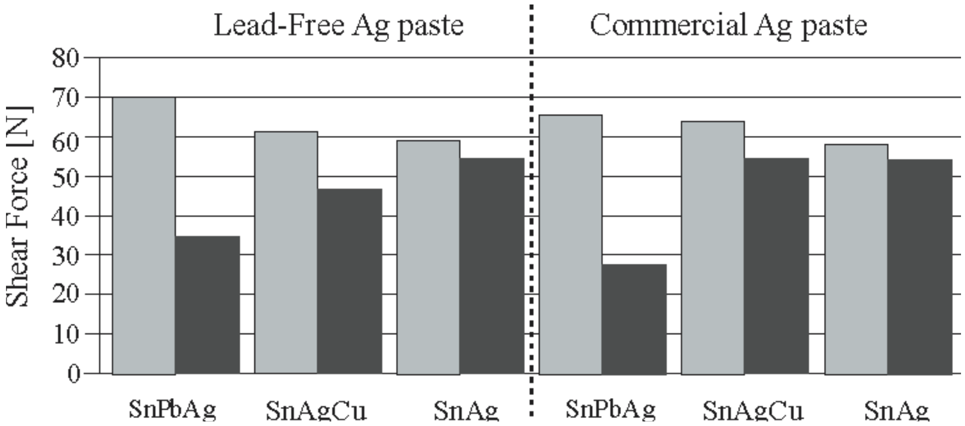


Fig. 24. Comparison of shear force for lead-free and lead-containing Ag thick films soldered with SnPb and lead-free alloys (initial adhesion – gray, adhesion after 48 hours aging at 150ºC – black).

Rys. 24. Porównanie wielkości siły ścinania dla srebrowych warstw grubych zawierających ołów i bezołowiowych lutowanych lutowiem SnPb i lutowiem bezołowiowym (adhezja początkowa – słupek szary, adhezja po starzeniu w 150ºC w ciągu 48 godz. – słupek czarny).

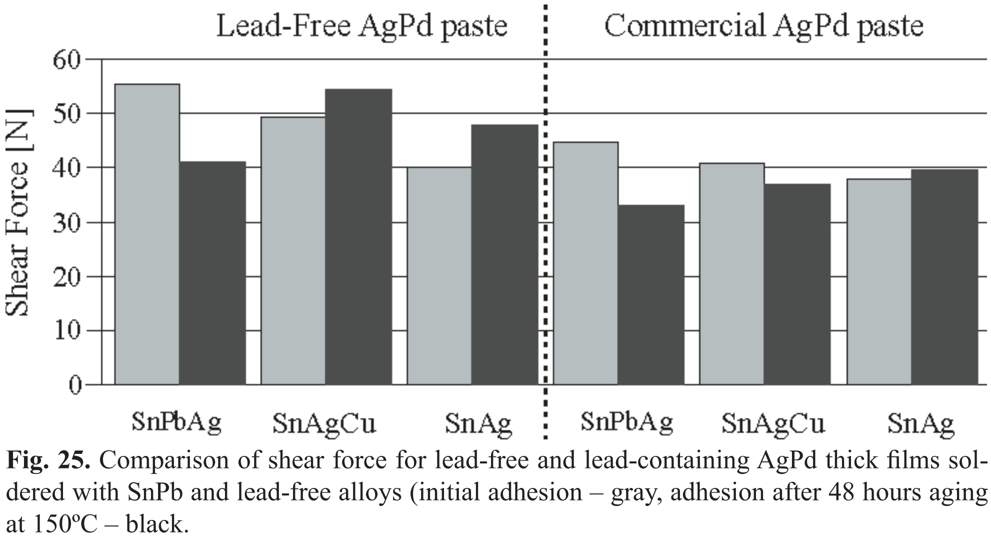


Fig. 25. Comparison of shear force for lead-free and lead-containing AgPd thick films soldered with SnPb and lead-free alloys (initial adhesion – gray, adhesion after 48 hours aging at 150ºC – black.

Rys. 25. Porównanie wielkości siły ścinania dla palladowo-srebrowych warstw grubych zawierających ołów i bezołowiowych lutowanych lutowiem SnPb i lutowiem bezołowiowym (adhezja początkowa – słupek szary, adhezja po starzeniu w 150ºC w ciągu 48 godz. – słupek czarny).

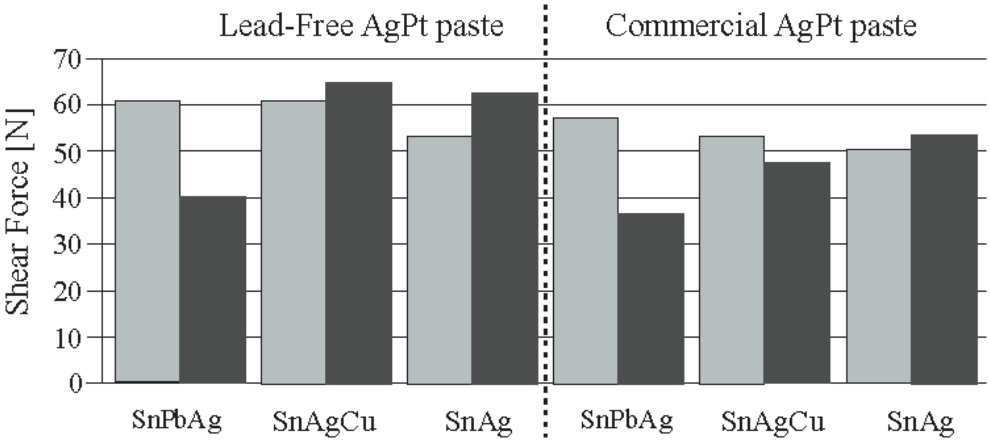


Fig. 26. Comparison of shear force for lead-free and lead-containing AgPt thick films soldered with SnPb and lead-free alloys (initial adhesion – gray, adhesion after 48 hours aging at 150ºC – black).
Rys. 26. Porównanie wielkości siły ścinania dla platynowo-srebrowych warstw grubych zawierających ołów i bezołowiowych lutowanych lutowiem SnPb i lutowiem bezołowiowym (adhezja początkowa – słupek szary, adhezja po starzeniu w 150ºC w ciągu 48 godz. – słupek czarny).

The results indicate that the lead-free solders are equally good as those containing lead. In case of lead-free solders the drop of adhesion after aging is much lower comparing with the traditional solders. Worth noticing is that on many occasions the adhesion after aging is higher than initial adhesion.

5. CONCLUSIONS

5.1. Formation of intermetallic compouds

Formation of the intermetallic compounds during the soldering and afterwards is a complex process. Actually, two separate, different in their nature stages can be distinguished. The first one, the soldering itself, when thick film is exposed to the molten solder, is short – takes just a few minutes. At this stage all the processes (diffusion, mass transfer and chemical reaction) are of liquid/solid state type. The second, is a very long one – lasting for all successful live of the solder joint. This time, after solidification, all processes are solid state/solid state reaction.

Worth noticing is that the first stage of soldering thick films differs essentially from that what occurs during soldering PBC copper. The reaction area of a solder on top of the Cu layer is approximately equal to the area of the solder drop placed on the layer. In case of thick film the reaction area might be much bigger, due to infiltration of the molten solder into the porous volume of conductor layer. The expanded reaction area may be larger by a factor up to 100%. The effective expansion of the reaction area is difficult to calculate. It mostly depends on porosity of thick film, but also on viscosity of the molten alloy at the given temperature, oxidation of the soldered surface, presence of glass traces, etc. Intermetallic compounds formation mechanism and kinetics is highly dependant on geometry of the layer – structure and distribution of pores. These processes are difficult to predict by simply applying growth kinetics to a quasi-one-dimensional layer geometry [22].

Solid state/solid state reaction, that is the second stage of IMC formation, requires direct mutual contact of two solid substances. This has been determined during the first stage of soldering. These reactions are, as all others, time, temperature and concentration dependent. However, solid state reactions are accompanied by the changes of co-ordinates of the reacting structure, what means that its geometry is important once again. The kinetics equation of two tablets pressed against each other, and heated, is completely different comparing with kinetics reaction of two equivalent mixed powders. Aging of solder joint belongs neither to two tablets type nor to mixed powders reaction. However, if there is any analogy, then PCB aging is more like two tablets case, and thick film – mixed powders case. The other thing which differs PCB soldering is chemistry on IMC, which in case of thick films is more complicated because of lager number of metals capable of forming IMCs present within the thick film layer.

5.2. Selection of lead free solders

There are well defined performance requirements for solder alloys used in microelectronics, and specifically - in thick film circuits. The solder must meet the expected level of electric and mechanical properties, and must also have the desired melting temperature. The latter property of a solder is especially important in thick film technology. A complex system of layers produced by sintering of variety of materials makes the TFCs susceptible to thermal shocks. Elevating the temperature of soldering might produce critical conflicts of TCE between all layers build into the TFC. Wettability and solder leaching depend on the properties of the employed alloy, as well as the properties of soldered thick film layer.

Lead is a very important part of solders used in electronics. Binary system 63Sn37Pb eutectic with a melting point 183ºC allows soldering conditions that are compatible with most thick film materials, substrates and devices. Lead provides many technical advantages to the SnPb solders:

1. Pb reduces the surface tension of pure tin (550 mN/m at 232ºC) down to 470 mN/m at 280ºC for 63Sn37Pb solder, facilitating wetting [12],
2. Pb reduces the melting temperature,
3. presence of Pb in a solder prevents transformation of white - β-tin to gray - α-tin upon cooling below 13ºC; the transformation results in a 26% increase of volume and causes loss of structure integrity, e.g. adhesion of solder to the conductor layer [13],
4. Pb serves also as a diluent enabling the other constituents of a solder such as Sn or Ag to form intermetallic bonds rapidly in the liquid state,
5. finally, lead being less expensive than tin, reduces the cost of solders.

When trying to identify an alternative to the currently widely used solders it is important to ensure that the replacing solders must be equal or superior to SnPb solders. The major performance characteristics of a solder that are important are manufacturability, reliability and environmental suitability. Manufacturability involves most of physical properties of a solder alloy relevant to solder such as surface tension, viscosity, density, melting point temperature, solderability, thermal and electric conductivity, corrosion and oxidation behavior, as well as re-workability and cost. Reliability of a solder alloy mostly depends on the TCE, elastic modulus, yield strength, shear strength, fatigue and creep behavior of the alloy.

The properties of solders that are important from a manufacturing and long-term reliability point of view are presented in Tab. 9.

Table 9. Important properties of solder alloys.
Tabela 9. Ważne właściwości stopów lutowniczych.

Properties relevant to manufacturing	Properties relevant to reliability and performance
Melting/liquidus point	Electrical conductivity
Wettability of diverse thick films	Thermal conductivity
Leaching of silver	Coefficient of thermal expansion (TCE)
Ability to be made in form of paste	Intermetallic compounds formation
Environmental friendliness	Tensile properties
Availability and number of suppliers	Shear properties
Manufacturability using current processes	Fatigue properties
Cost	Corrosion and oxidation resistance
Recyclability	Creep resistance

A relatively large number (over 70) of Pb-free solders have been proposed by a combination of researchers and manufactures. The majority of the alloys are based on Sn. Already in the late ‘90ies an attempt of selecting soldering alloy has been undertaken by Bastecki [12]. Certain alloys, selected by the author on the bases of their predicted properties, were sorted into two groups – those which should be excluded, and some should be retained. The results of this consideration are presented in Tab. 10.

Table 10. Lead free solders alloy selection [12].
Tabela 10. Propozycja wyboru bezołowiowych stopów lutowniczych [12].

Alloy Excluded/**Remaining**	Melting range (ºC)	Metal cost, US$/kg 2003/2004	Reason for exclusion
63Sn37Pb (std)	183	3.54/ 6.01	Pb content
62Sn36Pb2Ag	181	6.90/10.96	Pb content
42Sn58Bi	138	4.71/ 7.99	Bi content, MP too low for some applications
77.2Sn20In2.8Ag	179-189	31.15/52.89	In content, cost/availability
85Sn10Bi5Zn	168-190	4.92/ 8.35	Zn/Bi content, poor wetting broad freezing range
91Sn9Zn	199	4.81/ 8.17	Zn content, poor wetting
90Sn7.5Bi2Ag0.5Cu	186-212	6.90/11.72	Bi content, 4 component alloy, broad freezing range
96.3Sn3.2Ag0.5Cu	217-218	10.46/16.85	
95Sn3.2Ag1.5In	218	9.95/16.89	In content
96.2Sn2.5Ag0.8Cu0.5Sb	213-218	7.36/12.50	4 component alloy, no real benefit over binary alloys
96.5Sn3.5Ag	221	10.93/17/61	
98Sn2Ag	221-226	8.41/13.96	
99.3Sn0.7Cu	227	5.73/ 9.05	
97Sn0.2Ag2Cu0.8Sb	226-228	5.31/ 9.02	4 component alloy, no real benefit over binary alloys
95Sn5Sb	232-240	5.03/ 8.53	

Considering replacement of SnPb solders, one should realize the changes induced by application of a lead-free solder.

The immediate observation coming from studying the Tab. 10 is that all „remaining" solders have melting range much higher (217-227°C) comparing with the 63Sn37Pb eutectic (183°C). The melting point of a common solder 62Sn36Pb2Ag applied in TFT is even lower (181°C). This means that the soldering temperature must by elevated by minimum 20°C (or rather 30°C). Thermal shock of the soldered TFC will be more severe, eventually exposing more distinctly the mismatch of TCEs of different parts of the circuit.

In selecting a solder alloy to replace Pb bearing solders for use in thick film technology the following must be taken in consideration.

The solder should be binary or ternary. Quaternary alloys or composed of more parts should be avoided mainly because of growing complexity of intermetallic compounds formation. Thick films contain metals readily reacting with tin and other possible metals present in solders (Cu, In, Bi). That is why simplicity of solder alloys is in high value. Many researchers recommend using SnAg or SnAgCu solders with Ag content in the range 3.5 to 5%, and Cu content around 0.5%. According to several publications presence of Cu within the solder alloy slows down the growth of IMC layer [18]. The limitation of variables accompanying diffusion and intermetallic compound formation is another reason to use most simple soldering alloys.

The alloy should be near eutectic or eutectic, in order to keep the soldering process at the lowest possible temperature.

The alloy should have liqudus temperature low enough not to cause any damage to components or integrity of the thick film circuit (loss of adhesion).

The alloy must sufficiently wet the most common metals and metallizations used in thick film technology, which include copper, silver, palladium, platinum and their alloys.

The cost and availability of the alloy components must be considered also.

Preferred method of soldering thick film circuits is reflow of soldering pastes. The soldered metallization is exposed to a limited volume of molten solder. In case of dipping or especially wave soldering the metallization is facing semi-infinite volume of solder. This causes a very severe solder leaching condition. The dissolution of thick film metallization is accelerated by shear effect of flow of the molten solder.

The profiles of the solder pastes reflow do not require special precautions. According to several publications cited in this paper the researchers follow procedures recommended by the solder pastes manufacturers, which as a matter of fact are addressed to PCB assembling.

Presently, the experience of dealing with lead free solders in relation to thick film technology comes from research level. Data of lead free application in manufacturing are not available in the open literature.

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BEZOŁOWIOWE MIKROUKŁADY GRUBOWARSTWOWE

Wskazano położenie występowania ołowiu w układach grubowarstwowych. Wyróżniono dwie kategorie materiałów zawierających ołów: ceramiczne i metaliczne. Przedstawiono skróconą historię uwalniania materiałów ceramicznych od tlenków ołowiu. Omówiono przebieg reakcji pomiędzy lutowiem a materiałem warstw grubych, w czasie lutowania i po zestaleniu połączenia lutowniczego. Przeprowadzono porównanie przebiegu procesów lutowania warstw grubych ze zjawiskami zachodzącymi w czasie lutowania warstw miedzi w obwodach drukowanych. Przedstawiono propozycje użytecznych bezołowiowych stopów lutowniczych do lutowania warstw grubych wolnych od ołowiu.