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Chapter

Soldering by the Active Lead-Free Tin and Bismuth-Based Solders

Roman Koleňák, Martin Provazník and Igor Kostolný

Abstract

The chapter deals with Sn and Bi-In-based lead-free solders. The term "active solders" is used for the solders which contain one or more elements with enhanced affinity to some element contained in the substrate material. Mainly, Ti, In, lanthanides, etc. belong amongst the active metals. The role of an active element is to ensure a good wetting by a reactive decomposition of the surface layer of substrate. The perspective solders for joining the combined materials, as ceramics/metal, are mainly the tin-based, lead-free solders, which are enriched with titanium (usually up to 4 wt. %). The advantage consists in the fact that they offers a sufficient plasticity reserve, by what they are capable to compensate undesired residual stresses formed in the joint. Titanium also reacts with carbon, nitrogen or oxygen of the ceramic material, eventually it forms the intermetallic phases, which increase the strength of joint interface. The Sn-Ti, Sn-Ag-Ti and Bi-In-Sn solders were selected for the experiments. These solders were applied for fabrication of Al_2O_3 ceramics/Cu joints. The phase composition and microstructure of solders and soldered joints was analysed. Interactions in the interface of ceramic/solder and Cu substrate/solder were determined. The shear strength of soldered joints was measured

Keywords: active solder, ceramics, metals, ultrasonic soldering, shear strength

1. Introduction

1.1 Soldering with active solders

The term 'active solders' is occurring in the technologies oriented to fabrication of combined joints already for several decades. These solders contain an active element which reacts with the surface of the parent material during soldering process. This reaction takes place owing to the fact that an active element exerts higher affinity to the elements in the chemical composition of the substrate. The role of an active element is to ensure a good wetting of substrate with solder by reactive decomposition of the surface layer of the parent metal and by reducing the interfacial stress in the ceramics-solder interface. The active solder then may be used for fabrication of joints with different, either ceramic or metal, substrates. The most used active metals are titanium, zirconium or hafnium [1]. The chemical bonds in the interface of an active solder (with titanium content) and a solid substrate (ceramics/metal) are shown in **Figure 1**. Concentration of an active element should be sufficiently high in order to cause the wetting on a ceramic substrate, while it must not cause the formation of brittle intermetallic
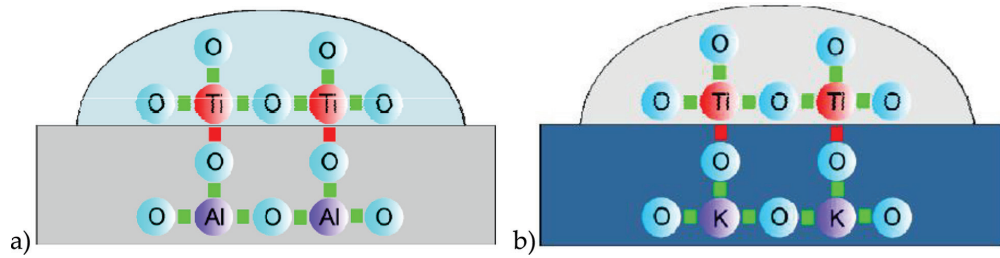
Figure 1.
Chemical bonds in the interface of (a) solder-ceramics, (b) solder-metal.

phases. Though a good wetting is achieved at higher content of active elements in a soldering alloy, nevertheless the joint then exerts poorer mechanical properties [2]. The commercially used active solders usually contain relatively small amounts of active elements (not more than 4 wt. %). Addition of indium to solder supports the wetting of substrate and lowers the soldering temperature and thus also the thermal expansivity of the fabricated joint [3]. The additional elements with higher affinity to oxygen (cerium and lanthanum) may protect the active solders against excessive oxidation of an active element during soldering in the air. At the same time also, the elements supporting wetting, for example, gallium [4, 5], are added to active solders.

The active element is moved from the entire solder volume to both soldered materials during the soldering process. Thus, a reaction layer in the thickness of several μm, containing the reaction products of an active element and substrate, is formed in the interface of soldered joint. The thickness of this reaction layer depends on the solder type and soldering conditions. The active element with a high affinity to oxygen, which reacts with the ceramics during soldering, creates the bonds in an interatomic level. The active element (e.g. Ti) contained in the solder bonds the oxygen from the surface layers of oxide ceramics. The following oxide types are formed on the ceramics by the reaction of an active element: TiO, Ti_2O_3, Ti_3O_5, Ti_4O_5 and TiO_2. The reaction product alters the surface energy of ceramics and enables wetting of the solder [6]. The following type of reaction takes place between the active element and Al_2O_3 ceramics [7].

$$M/AO_x \rightarrow M/mMA_a/nM_bA_cO_d/AO_x$$

where
M   metal element of the solder/interface.
AO_x ceramic element
O   may be an oxide
n   different combined oxides
M   different intermetallic compounds

This type of chemical reaction is valid for the active soldering with an active element as Ti, Zr and/or Hf. The layer formed after such a reaction will depend on the soldering parameters (temperature and time) and environment atmosphere (vacuum oven and inert gas). For the active element Ti on Al_2O_3 substrate, it is valid [7]:

$$Ti/Al_2O_3 \rightarrow Ti/Ti_3Al/TiAlO_x/Al_2O_3$$
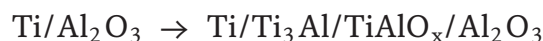
In the selection of an active element for soldering ceramic materials, it is necessary to take into account the fact that higher concentration of an active metal may result in joint embrittlement. This is caused by the formation of brittleness phases in the ceramic-solder zone [8].

The use of Ti as an active element in a solder has been investigated by many authors. Titanium in the $SnAgTi_4$ solder provided a reduction in the wetting angle to the sapphire substrate. The absorption of Ti together with the release of Al from the sapphire substrate provides an interaction between the solder and the substrate [9]. Another investigated aspect of the Sn-Ag-Ti-based solder was its spreadability on porous graphite when applying ultrasonic vibrations. The authors' results [10, 11] have shown that the application of ultrasonic waves during soldering allows the active solder to spread on the surface of the graphite at a relatively low temperature under atmospheric conditions. The oxide layer on the molten solder forms a compact layer of a certain thickness which prevents the liquid solder from wetting the base material. The reduction of Ti oxide formation is possible by the addition of Y, as documented by the authors [12]. They found that the oxide layer of the solder consists mainly of titanium dioxide. A small amount of Y improves the resistance to oxidation because it suppresses the oxidation of Ti in the molten solder and reduces the amount of oxygen atoms entering the molten solder. The composition of the surface oxide of $SnAg_4Ti_2Y_{0.5}$ solder was mainly Y_2O_3 and a low amount of titanium dioxide. After ultrasonic application, the oxide layer was disrupted, and the solder was able to wet the materials. The authors found that the spreadability and wettability of Sn-Ag-Ti-based solders on the graphite substrate could be improved by increasing the time of ultrasound activation. Similar observations were published in [13], where the authors deal with the soldering of aluminium-graphite composite material using a $SnAg_{3.5}Ti_4Cu_{0.5}$ solder at soldering temperature of 250°C. Aluminium from the composite was dissolved in the active solder and formed a solid solution of Al-Ag-Sn at the interface. The average shear strength of the Al-Gr/Al-Gr joints was 8.15 MPa.

The main factors affecting the solder selection comprise different melting points of soldered materials, different surface stresses of the substrates and the residual stresses formed during solidification process. Therefore such a solder is proposed where the matrix exerts a sufficient plasticity reserve, capable to compensate the residual stresses formed in the joint [14]. To overcome the mentioned problems, the solder meeting a complex set of desired criteria for the quality of resultant joint is selected. The active solders, similarly as the commercial solders, are classified by the melting temperature to solders, brazing alloys and high-temperature solders. The active solders are further classified by the mechanism of bond formation to high-temperature and mechanically activated ones. For reaction capacity of an active element, the soldering temperature in the case of high-temperature-activated solders must be higher than 780°C. The classification of active solders and their chemical composition is shown in **Table 1**.

1.2 Active solders

The primary materials of an active solder are usually tin, lead, bismuth, zinc or indium and the alloys based on these metals. Active solders allow to join also unusual combinations of metallic materials (e.g. CrNi steel, Mo, W, Ti, Cr, etc.) and non-metallic materials as siliceous glass, sapphire, carbon, silicon and several types of ceramics. In soldering with active solders, the solder is capable to compensate the stresses formed due to different thermal expansivity of joined materials by its plastic strain, shear mechanism or yield. In such a manner, the highest reduction of residual stresses may be achieved at a preserved joint stability. In the case of soldering untraditional material combinations with extremely different coefficients of thermal expansivity (e.g. glass with aluminium/copper), heavier solder thickness should be selected, in order to prevent the cracks in the joint interface. Such joints are used mainly in electrotechnics, where lower strength and thermal resistance of joint are sufficient. These solders also allow to fabricate the

Active solders	Application temperature	Chemical composition
Solders	From cryogenic temperatures up to 200°C	High-temperature activation, based on Sn, In and Pb (e.g. $Sn_{90}Ag_{10}Ti_3$)
		Mechanical activation based on Sn (e.g. $SnAg_{3.5}Ti_4(Ce,Ga)$)
Brazing alloys	Up to 400°C	Based on Ag, Cu and Au (e.g. $Ag_{72}CuTi_{1.5}$)
High-temperature solders	Up to 900°C	Based on Ni, Co, Pd and Pt (e.g. $Ni_{70}Hf_{30}$)

Table 1.
Classification of active solders by the melting point.

vacuum-tight joints used in the vacuum and cryogenic technology, where indium-based solder has proved as suitable. The solders containing lead are not suitable for soldering in vacuum, since considerable evaporation of lead and also oven contamination may occur. In the case of soldering with lead, it is necessary to employ the through-flow atmosphere of pure argon, eventually helium [15]. The active solders may be activated mechanically (by scrapping or ultrasound) in dependence on material which they wet (metal/ceramics) within the temperature interval from 200 to 400°C. An essential group of these solders applicable at lower soldering temperatures comprises the tin-based, lead-free solders which are enriched by a small amount of an active element as titanium. An example of such active solders destined for soldering a wide scope of materials is the solders type S-Bond, where also $SnAg_{3.5}Ti_4(Ce,Ga)$ solder [16, 17] may belong.

Titanium is moved from the solder matrix to the interface; combines with carbon, nitrogen or oxygen from the ceramic material; and thus creates intermetallic compounds which allow the wetting of ceramic substrate and creation of a metallurgical bond. Fluxless soldering process in the air is concerned, where no corrosion owing to flux remnants occurs [18, 19].

The active solders for high-temperature activation necessitate considerably higher soldering temperature and may be used only in a vacuum and/or shielding atmosphere. Soldering temperature of the tin- and lead-based solders varies within 850–950°C. The solders for mechanical activation (e.g. $SnAg_{3.5}Ti_4(Ce,Ga)$) may be used also for high-temperature activation. However, greater wetting angles than in the case of mechanical activation are attained [14]. As an example of using S-Bond 220-1 ($SnAg_{3.5}Ti_4(Ce,Ga)$) solder in electrotechnics, joining of Al_2O_3 with copper in **Figure 2** may be mentioned. This solder allows to join the materials with different
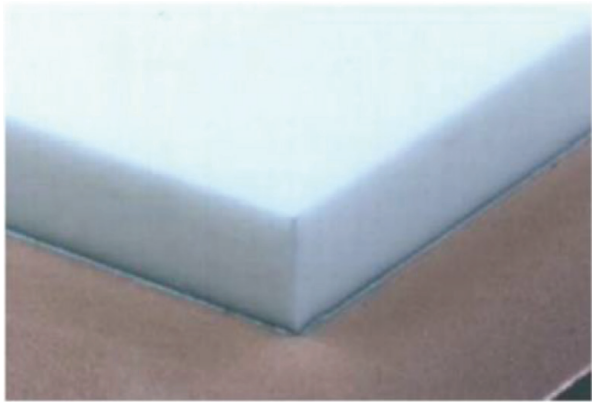

Figure 2.
Detailed view of Al_2O_3-Cu joint fabricated with S-Bond solder [20].

coefficients of thermal conductivity and expansivity (metals, light metals, ceramics, composites with metal matrix, carbides, glass, etc.) [20].

The solder type S-Bond contains Ti as an active element and elements from the group of lanthanides. These active elements migrate to the interface of the soldered joint and act upon the material surface by the active disruption and removal of oxides. Disruption of oxide layer, which prevents the formation of contact between the solder and substrate surface, is called as 'activation'. As soon as the oxide layer is disrupted, the solder volume reacts with the substrate surface, and a strong bond with the joined surface is thus formed.

The bond is formed by two mechanisms:

- *Metallurgic bonding*—for example, with Cu and/or Al surfaces. Besides the active element, also other elements of solder, as Sn-Ag-Ti, react with the substrate elements. These contribute to bond formation by creation of phases as Al-Ti, Cu-Sn, Ag-Sn, etc. system. This process may be used for a wide scope of metallic materials.

- *Gravity bond*—in the case of metals with very thin dielectric surface oxides. These are, for example, Ti or stainless steel with TiO_2 eventually Cr_3O_2 oxides. Bonding is ensured by the gravity of surfaces with opposite electric charge. The active elements of solder and the elements of joined substrate are attracted across the interface by the van der Waals forces.

1.2.1 High-temperature activation of an active solder

In the case of active solders containing Ti (or other reactive elements), the high-temperature activation in shielding atmosphere of vacuum is employed. The active element reacts with the surface oxides of substrates at the soldering temperatures of 850–950°C. Similarly also nitrides, carbides or silicides of the active element are formed in the solder in the case of non-oxide ceramics. One of the greatest disadvantages of this process consists in the necessity of a vacuum.

The work cycle in **Figure 3** consists of a rapid heating to soldering temperature, dwell time for about 9 minutes and a long free cooling down (for about 320 minutes) in the oven. The short dwell time at the soldering temperature prevents formation of brittle phases and grain coarsening. The slow cooling down is needed in order to prevent high residual stresses, which may cause the joint cracking.

The diffusion processes take place during slow cooling down, which will be exerted in the growth of diffusion zone in the parent metal and the solubility zone in the solder. Soldering with an active solder may be performed in a vacuum furnace at
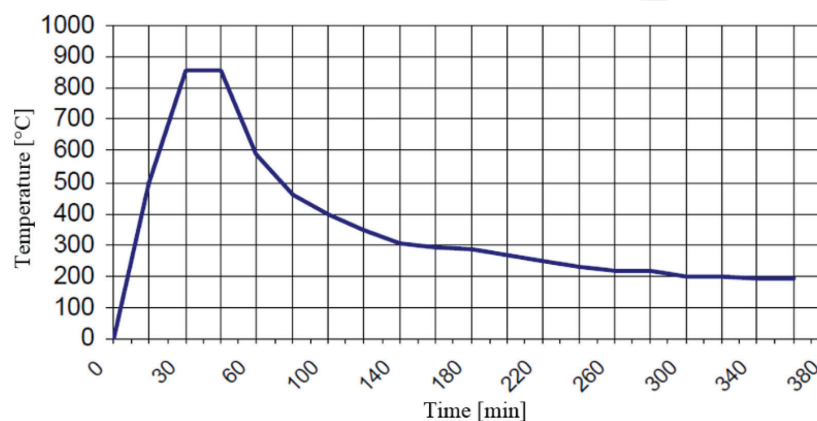

Figure 3.
Scheme of thermal cycle of vacuum soldering [21].

the pressure of 10^{-1}–10^{-3} Pa. In some special cases, soldering may be performed also in the overpressure of argon or helium. Nitrogen cannot be used as a shielding gas since it deteriorates the wetting of ceramics. This is caused by the fact that nitrogen has a high affinity to Ti, and thus it depletes the solder by Ti. The high-temperature activation cannot be used for soldering of metallic materials with the coatings of Au, Ag, Cu, Al and Mg, which exert a high dilution rate in Sn solder. The working parameters exert a significant effect upon the properties of soldered joints [21].

1.2.2 Mechanical activation of solder

Mechanical activation seems to be a new trend in the field of active solders at present. Soldering is realised at temperatures of 250–280°C with the dwell time from 30 seconds up to 3 minutes. The time- and power-demanding high-temperature activation is in this process replaced with the mechanical activation of an active element. In this way, the necessity of a vacuum, shielding atmosphere or multistep solder deposition is eliminated [21].

Mechanical activation may be realised by:

- scratching

- spreading with a metal brush

- vibrations

- ultrasound

The primary reason for activation consists in the fact that the surface of metallic materials is covered by an oxide layer, which must be gradually disrupted during the soldering process. Activation of surface layers on ceramic materials is possible exclusively by the application of ultrasound.

In order to allow soldering in the air without the necessity of flux, the active solder is alloyed with the elements from the group of lanthanides. These are the rare earth metals, for example, Ce and Ga, which protect Ti against oxidation during heating and soldering [22]. The soldered joint fabricated with $Sn_{3.5}Ag_4Ti(Ce,Ga)$ solder is shown in **Figure 4**.

The work cycle of soldering with ultrasound activation is considerably shorter than in the case of high-temperature activation. The soldering temperatures are also significantly lower than at high-temperature activation. The structure of soldered materials is less affected, and therefore lower residual stresses are formed.
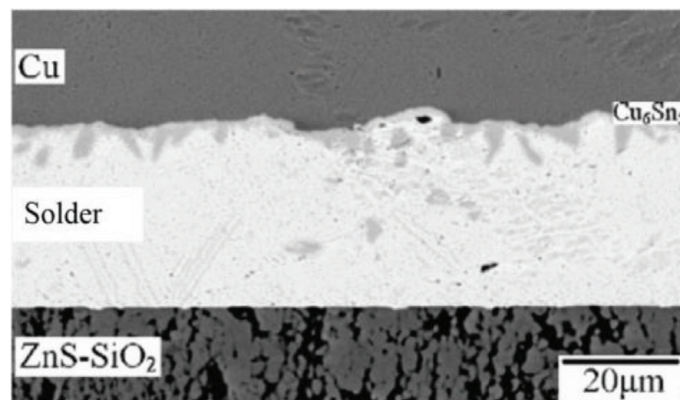

Figure 4.
Interface of ZnSiO$_2$, Sn$_{3.5}$Ag$_4$Ti(Ce,Ga), Cu joint [23].

1.3 Activation mechanism of an active element by ultrasound

The surface of soldered materials is covered with an oxide layer which must be gradually disrupted during soldering. This is performed by the mechanism called 'solder activation'. For the soldering of metals, it is mostly sufficient to activate mechanically by scratching; however, in the case of ceramic materials, it is necessary to employ the ultrasonic activation with the frequency over 20 kHz.

Mechanical activation is realised by:

- scratching and spreading with a metal brush (suitable for soldering metals as Cu, Al, Ni, CrNi steel, etc.)

- vibrations (50–60 Hz)

- ultrasound with the frequency over 20 kHz (suitable for soldering ceramic and non-metallic materials)

The most used technologies for fabrication of combined soldered joints type ceramics-metal are derived from ultrasonic soldering. This results from the finding that only ultrasonic activation is sufficiently efficient for disrupting the surface layers on ceramic materials [15, 21]. The physical principle of ultrasonic soldering consists in the fact that cavitation of sufficient intensity occurs in liquids and molten metals affected by ultrasonic field. The erosive activity of cavitation attacks, disrupts and removes the oxides from the surface of the soldered part. If a solder with a sufficient content of active elements is used, the reliable, diffusion and metallurgical bonding with the parent material is attained. Ultrasonic cavitation reduces the surface tension and enhances the spreadability and capillarity of solders. It also significantly affects the distribution of an active element in the solder matrix and supports the diffusion processes in the phase interface. The time of solder activation by ultrasound partially depends on the resistance of surface oxide layers against the cavitation erosion. However, the times of working cycles are incomparably shorter than the times of activation at high temperatures in vacuum. Application of ultrasonic method is sometimes limited by the soldering material used. In the case of brittle substrates, the damage of specimen by cracking the surface layers may occur [24].

1.3.1 Principle of solder activation by power ultrasound

Majority of power ultrasound applications, where also ultrasonic soldering belongs, necessitate semi-wave transducers with the resonance frequencies of 20–60 kHz. Ultrasonic transducer transfers the electric power to mechanical—the so-called ultrasonic—oscillations. Ultrasonic head consists of an oscillating system fastened in a case made of plastic. The protective case serves for an ergonomic grasping of the tool, eventually its clamping on a stand. The oscillating system is formed by a piezoelectric transducer, a concentration adapter and an exchangeable working tool. The exchangeable tools—sonotrodes—which are screwed on the adapter may be of different shapes. In most cases it is a conical point made of titanium alloy [25]. The principal scheme of an equipment for ultrasonic soldering is shown in **Figure 5**.

The sonotrode point is oscillating with the frequency of alternating current supplied by the generator through the connecting cable. The amplitude of oscillation is variable, and it is altered with the frequency of the supplied current. It generally varies at the level of 10^{-4} mm. The rate and intensity of applied UT oscillation vary within a certain range, and it is selected with regard to the process conditions and the character of materials. In this way, it is possible to affect both the strength characteristics of the
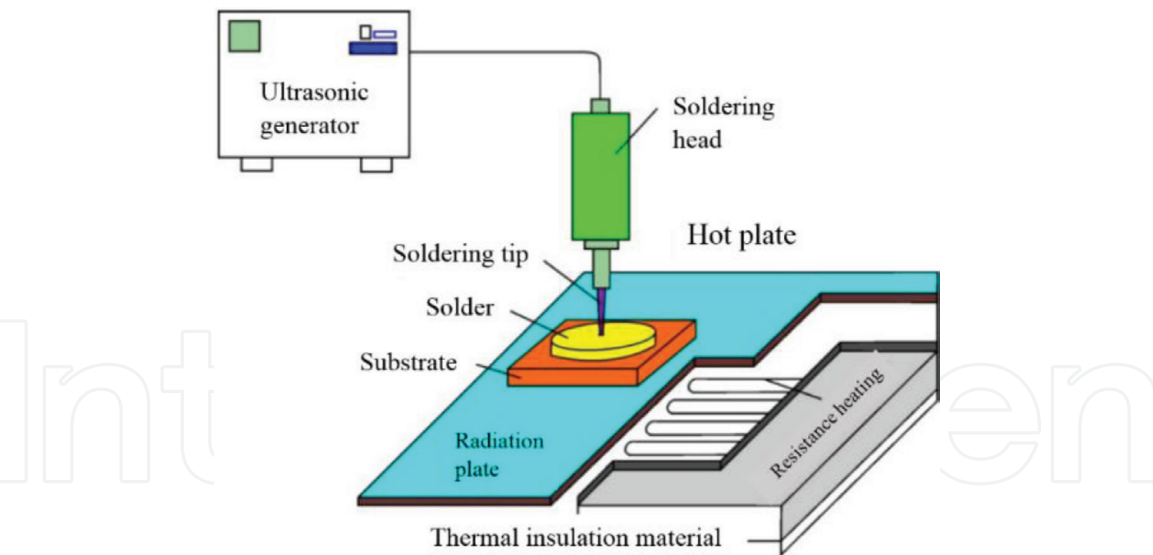
Figure 5.
Principal scheme of an equipment for ultrasonic soldering.
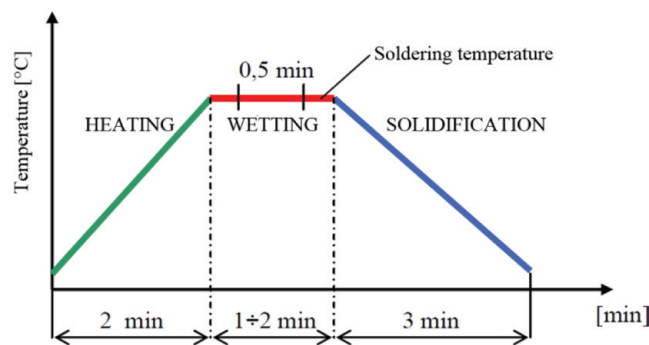

Figure 6.
Work cycle of soldering with application of mechanical activation.

joint and its technological parameters (e.g. the joint width) as well [26]. The work cycle of soldering with application of mechanical activation by ultrasound is roughly 10 times shorter than in the case of high-temperature activation (**Figure 6**).

Acting upon the active solder by ultrasound may be performed in several ways. The technology depends on the size and geometry of the joint, soldering temperature, type of parent metal, number of produced pieces and other parameters. The most used technique of laboratory activation of melts by ultrasound comprises the method, where the solder is molten on the surface of a joined unit by an external heat source, and the ultrasonic power is supplied through the solder from a sonotrode point on the part surface. This method makes it possible to solder selectively the localised surfaces on large parts or to cover the entire surfaces of parts. This principle is shown in **Figure 7** [24].
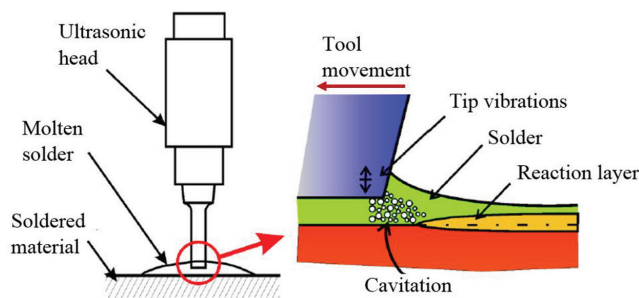
Figure 7.
Manual soldering with ultrasound assistance.

2. Active solders for ultrasonic activation

2.1 SnTi$_2$ solder

Figure 8 shows the microstructure of SnTi$_2$ solder. This solder was manufactured by free casting in a vacuum. The solder exerts heterogeneous composition. The matrix consists of 100% Sn. The round, dark and oblong grey phases are the intermetallic compounds of the Ti-Sn system. The zones of solder containing 35.2% Ti and 64.8% Sn consist of Ti$_6$Sn$_5$ phase. Composition of SnTi$_2$ solder in the selected spots is shown in **Table 2**. Diffraction analysis performed on a sample of SnTi$_2$ (**Figure 9**) solder has revealed the presence of the following phases: Ti$_6$Sn$_5$, Ti$_3$Sn, Sn$_3$Ti$_5$ and Sn$_5$Ti$_6$. Solder microstructure consists of a tin matrix (100% Sn) with non-uniformly distributed phases of the Ti-Sn system. The coarse dark-grey phases in **Figure 8** represent the Ti$_6$Sn$_5$ phase; the smaller bright-grey phases with Sn designation contain 3.6% Ti and 96.4% Sn.

2.2 SnAg$_{3.5}$Ti$_4$(Ce,Ga) solder

The SnAg$_{3.5}$Ti$_4$(Ce,Ga) solder shown in **Figures 10** and **11** consists of a tin matrix with non-uniformly distributed constituents of intermetallic phases of binary Ti-Sn, Ag-Sn and Ag-Ti systems. The dark-grey phases contain an average of 31.5% Ti and 68.5% Sn, while the constituents of the Ti$_6$Sn$_5$ phase are concerned. The dark, clearly limited zones are formed by almost pure Ti. The composition of SnAg$_{3.5}$Ti$_4$(Ce,Ga) solder in the selected spots is shown in **Table 3**.
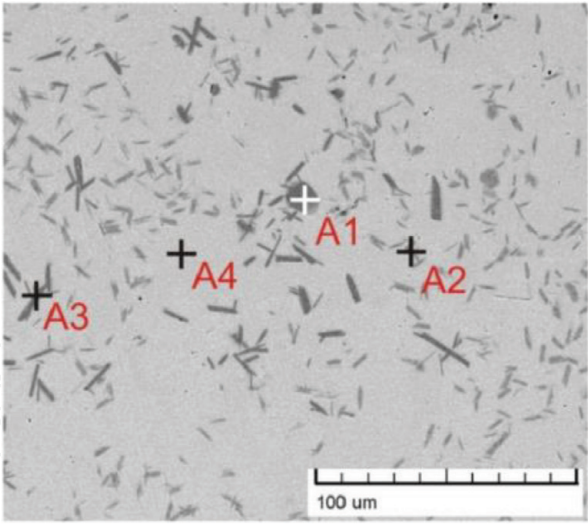

Figure 8.
Microstructure of the binary Ti-Sn system (SEM).

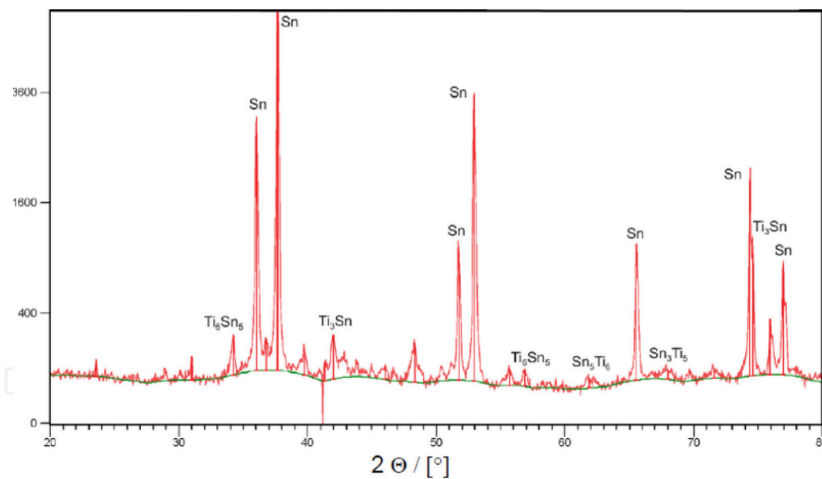|	Ti [wt. %]	Sn [wt. %]
A1	35.2	64.8
A2	4.36	95.64
A3	13.8	86.2
A4	0	100

Table 2.
Solder composition.

Figure 9.
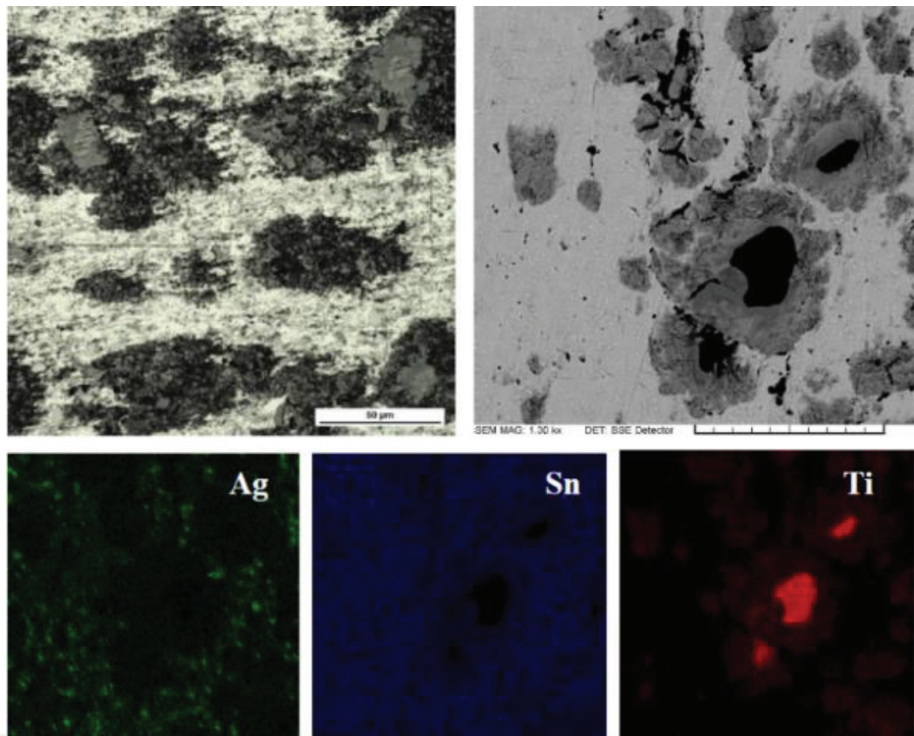*X-ray record of SnTi$_2$ solder.*

Figure 10.
Microstructure of SnAg$_{3.5}$Ti$_4$(Ce,Ga) solder (SEM) + concentration profiles of elements.

Figure 12 shows the record of the diffraction analysis of SnAg$_{3.5}$Ti$_4$(Ce,Ga) solder. The following phases were revealed: Ti$_6$Sn$_5$, Ag$_3$Sn, Ag$_3$Ti and Ti$_2$Sn. The solder consists of a tin matrix with non-uniformly distributed constituents of intermetallic Ti-Sn phases and the constituents of Ag$_3$Sn and Ag$_3$Ti (93% Sn, 6.5% Ag, 0.5% Ti) phase. The dark-grey phases shown in **Figure 11** in average contain 31.5% Ti and 68.5% Sn, while the Ti$_6$Sn$_5$ phase is concerned. The dark zones are composed of 100% Ti.

2.3 Bi-In25Sn18 solder

Figure 13 shows the microstructure of bismuth-based BiIn25Sn18 solder of eutectic composition. The solder was manufactured in the form of cast ingot. It exerts a fine multi-crystalline structure. All phases are uniformly distributed in the solder, without any traces of formation of conglomerates and/or clusters causing the heterogeneity in the chemical composition of solder elements. Composition
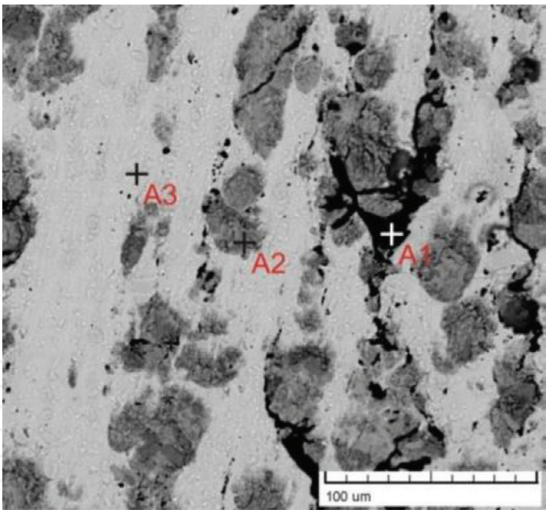
Figure 11.
The SnAg$_{3.5}$Ti$_4$(Ce,Ga) solder (SEM).

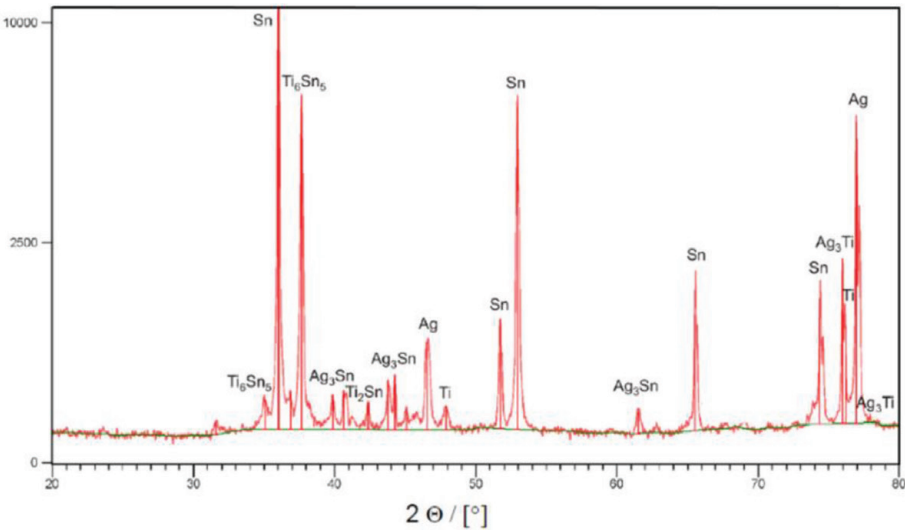|	Ti [wt. %]	Ag [wt. %]	Sn [wt. %]
A1	99.15	0	0.85
A2	31.08	0.73	68.19
A3	0.5	6.56	93.14

Table 3.
SnAg$_{3.5}$Ti$_4$(Ce,Ga) solder composition.

Figure 12.
X-ray record of SnAg$_{3.5}$Ti$_4$(Ce,Ga) solder.

of the selected zones in BiIn25Sn18 solder is shown in **Table 4**. The ternary
Bi-In-Sn system exerts two eutectics with a very low melting point. The composi-
tion of BiIn25Sn18 solder is very close to a ternary eutectics of Bi-In-Sn system,
with a melting point of 77.5°C. Diffraction analysis performed on a specimen of
BiIn25Sn18 solder (**Figure 14**) has revealed the presence of the following phases: Bi,
Sn, In, BiIn$_2$, In$_3$Sn, InSn$_4$, BiIn and Bi$_3$In$_5$. The solder exerts very fine and uniformly
distributed multiphase structure. The grey matrix contains in average 80% Bi,
12.5% In and 7.5% Sn. The white phase is composed of Bi-In (32.5% In and 67.5%
Bi) constituents, while the Bi-In phase is concerned. The dark-grey constituents in
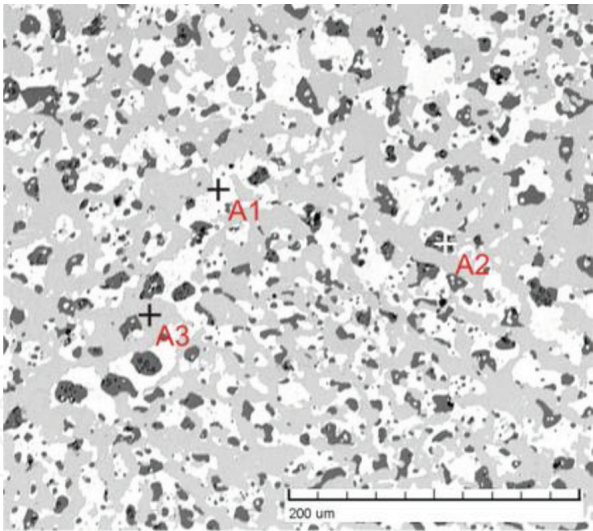**Figure 13** show an increased tin content (13.5% Bi, 6.5% In, 80% Sn).

Figure 13.
The BiIn25Sn18 solder (SEM).

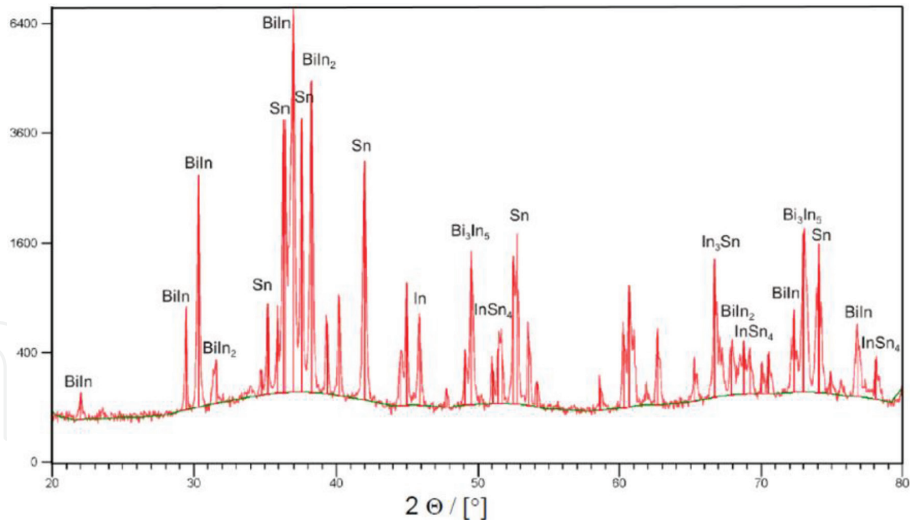|	Bi [wt. %]	In [wt. %]	Sn [wt. %]
A1	80.55	12.3	7.15
A2	11.7	0	88.3
A3	64.5	35.5	0

Table 4.
BiIn25Sn18 composition.

Figure 14.
X-ray record of BiIn25Sn18solder.

2.4 Results of shear strength

Figure 15 shows the values of shear strength of the analysed joints fabricated with $SnTi_2$, $BiIn_{25}Sn_{18}$ and $SnAg_{3.5}Ti_4(Ce,Ga)$ solders. The values give the average results of three measurements performed for each type of joint.

The highest strength on the copper and ceramic substrate was achieved with $SnAg_{3.5}Ti_4(Ce,Ga)$ solder. On the Al_2O_3 ceramics, it attained the strength of 33 MPa, while on the copper, it was 35 MPa. In the case of this solder, the difference between the shear strength values on the side of ceramics and the copper was smallest from amongst
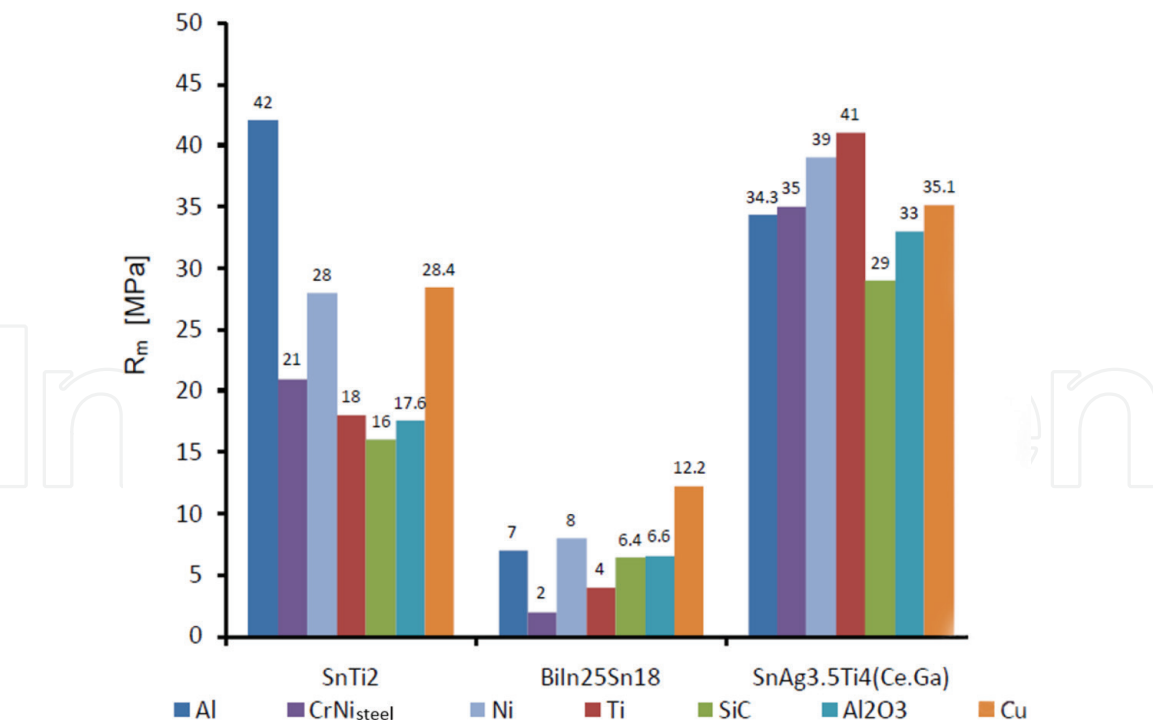
Figure 15.
Shear strength of SnTi$_2$, BiIn$_{25}$Sn$_{18}$ and SnAg$_{3.5}$Ti$_4$(Ce,Ga) solders.

all solders. The lowest shear strength values were attained with BiIn25Sn18 solder, both on the side of copper (12.2 MPa) and on the side of Al$_2$O$_3$ ceramics (6.6 MPa). The average shear strength values of SnTi$_2$ solder varied within the range from 16 to 42 MPa.

3. Analysis of soldered joints

3.1 Analysis of Al$_2$O$_3$-BiIn25Sn18 joint

Figure 16 shows a combined soldered joint of BiIn25Sn18-Al$_2$O$_3$ ceramics. A longitudinal crack was observed in the interface of BiIn25Sn18-Al$_2$O$_3$ joint, which has occurred along the entire specimen length. This crack was formed during the metallographic preparation of specimen due to poor plastic-elastic properties of the solder used.
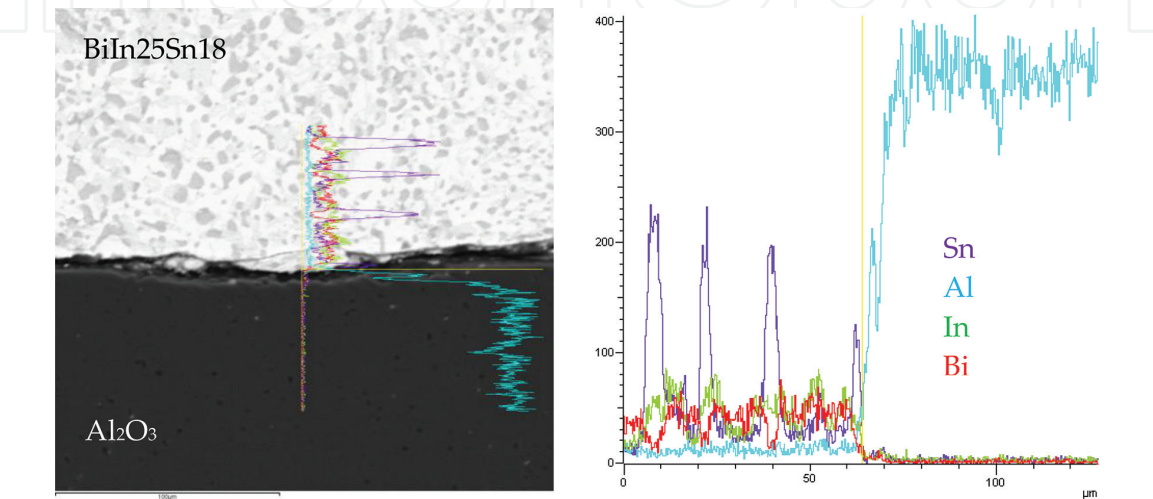
Figure 16.
Interface of Al$_2$O$_3$-BiIn25Sn18 joint (SEM) + concentration profiles of elements.
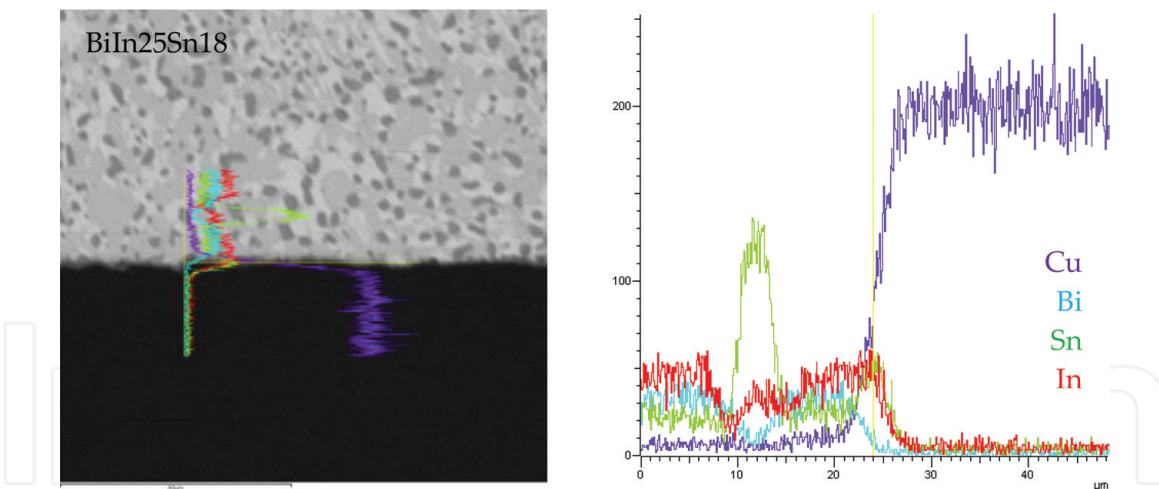
Figure 17.
Interface of Cu-BiIn25Sn18 joint (SEM) + concentration profiles of elements.

Based on the performed SEM and EDX analyses, it can be supposed that In primarily contributes to bond formation by creating indium oxide—In_2O_3. Besides In, Bi also partially contributes to bond formation. The presence of Sn is indifferent, and it does not exert any effect on the bond formation. Its presence was revealed in the grey phase. The interface contains exclusively a pale matrix composed of Bi and In. The formed reaction products are brittle with poor toughness that caused the crack formation in the bond plane.

3.2 Analysis of Cu-BiIn25Sn18 joint

Figure 17 shows the interface of BiIn25Sn18-Cu joint. In the interface of BiIn25Sn18 solder and copper, a noticeable increase in the proportion of the darker phase, formed mostly of Sn, may be seen. A continuous transition zone of reaction elements is formed in the solder interface. Based on the study of binary diagrams and performed analyses, formation of the following phases is supposed: Cu_3Sn, Cu_6Sn_5 and Cu_9In_4. A thinner, non-wettable phase rich in Cu (Cu_3Sn), which is followed with Cu_6Sn_5 phase, is formed in the joint interface. From the map of quantitative proportion of chemical elements, it is obvious that in the copper-solder interface mainly, the presence of In and Sn is exerted. However, Bi does not play any significant role in bond formation and does not create any phases with copper.

3.3 Analysis of Al_2O_3-$SnAg_{3.5}Ti_4$(Ce,Ga) joint

Figure 18 shows the interface of Al_2O_3-$SnAg_{3.5}Ti_4$(Ce,Ga) joint. A continuous reaction layer containing Ti was observed in the interface of Al_2O_3-$SnAg_{3.5}Ti_4$(Ce,Ga) joint. This reaction layer allows the wetting of ceramic material and the tin-silver matrix of solder guarantees the desired strength and sufficient plastic properties of soldered joint to compensate the strains and stresses formed during cooling down. Slightly increased concentration of cerium was also observed in the joint interface. The presence of gallium and/or its effect upon bond formation was not observed (**Figure 19**).

3.4 Analysis of Cu-$SnAg_{3.5}Ti_4$(Ce,Ga) joint

Figures 20 and **21** show the interface of Cu-$SnAg_{3.5}Ti_4$(Ce,Ga) joint. A continuous layer of reaction elements is formed in the interface of solder and copper. Primary effect upon bond formation is exerted by Sn. Cu is dissolved in Sn matrix
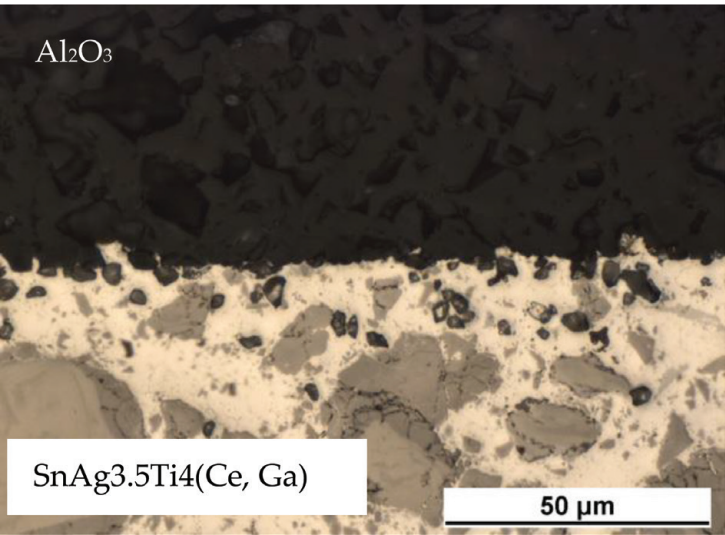
Figure 18.
Microstructure of interface of Al_2O_3-$SnAg_{3.5}Ti_4(Ce,Ga)$ joint (SM).

Figure 19.
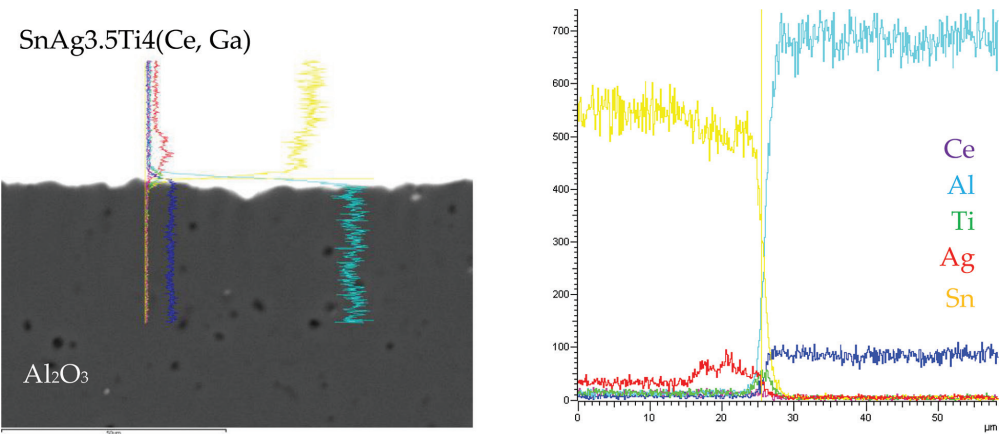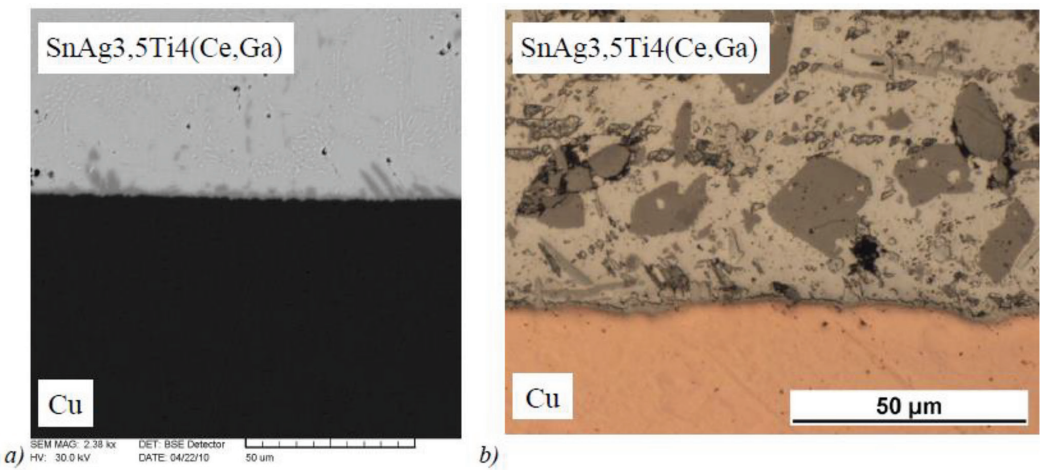*Interface of Al_2O_3-$SnAg_{3.5}Ti_4(Ce,Ga)$ joint (SEM) + concentration profiles of elements.*

Figure 20.
Microstructure of interface of Cu-$SnAg_{3.5}Ti_4(Ce,Ga)$ joint (a) (SEM) and (b) (SE).

and forms the Cu_3Sn and Cu_6Sn_5 phases which grow in the direction from the phase interface to solder matrix. Similarly to the case of soldering Al_2O_3, rapid dilution on the side of parent materials has not occurred. Sn matrix prevails in the solder, while the darker zones are formed by binary alloys of Sn with Ti and/or Ag.
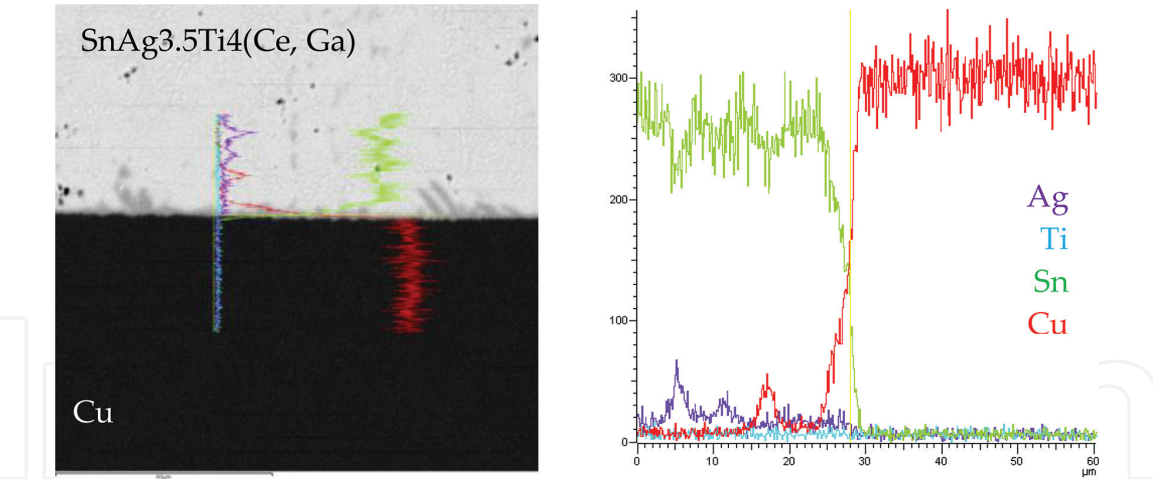
Figure 21.
Interface of Cu-SnAg₃.₅Ti₄(Ce,Ga) joint (SEM) + concentration profiles of elements.

It was found out that Ti does not contribute at all in bond formation and its effect upon bond formation was unobservable. Ag element did not exert any significant interaction with the parent material; however, its presence in the interface was observed. The Ce and Ga elements occurred in the boundary in such low amounts that they could not be identified at all.

3.5 Analysis of Al_2O_3-$SnTi_2$ joint

Figure 22 shows the interface of $SnTi2$-Al_2O_3 joint. From the map of planar distribution of elements, it is obvious that the active Ti element significantly contributes in bond formation. It forms a continuous reaction layer, similarly as in the case of $SnAg_{3.5}Ti_4(Ce,Ga)$ solder. This reaction layer is formed by Ti reaction with oxygen from ceramics at formation of titanium oxides, which alter the surface tension of ceramics and thus allow its wetting by solder. The effect of other elements (except Ti) upon bond formation was not observed (**Figure 23**).

3.6 Analysis of Cu-$SnTi_2$ joint

Figure 24 shows the interface of $SnTi2$-Cu joint. A continuous layer of reaction elements is formed in the interface of $SnTi_2$ solder and copper by dissolving Cu in
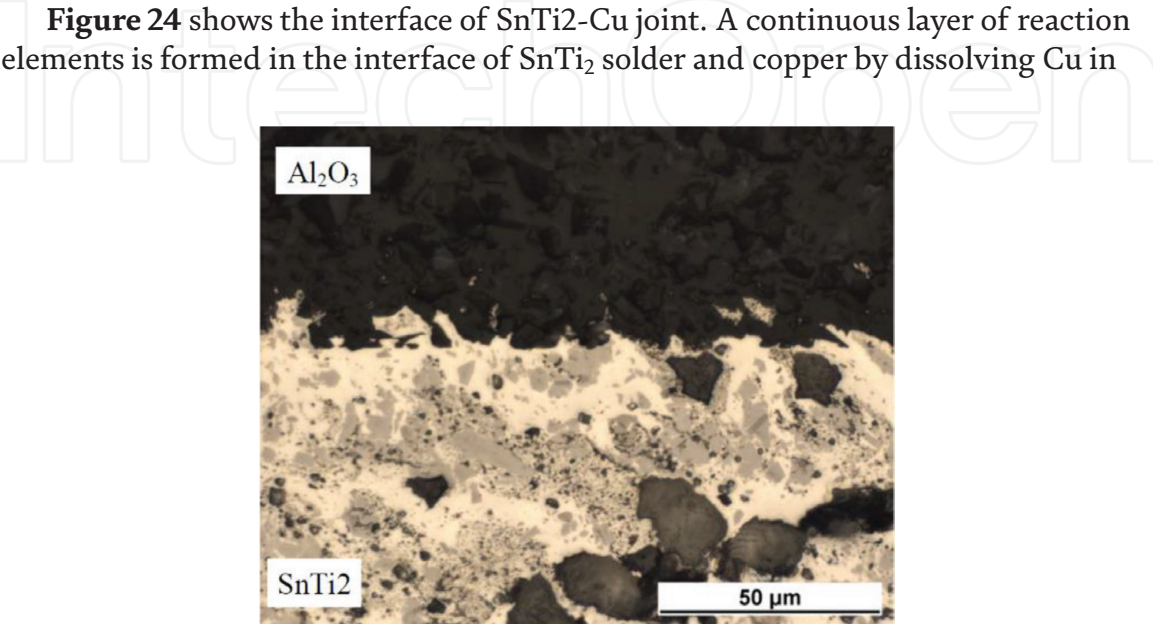

Figure 22.
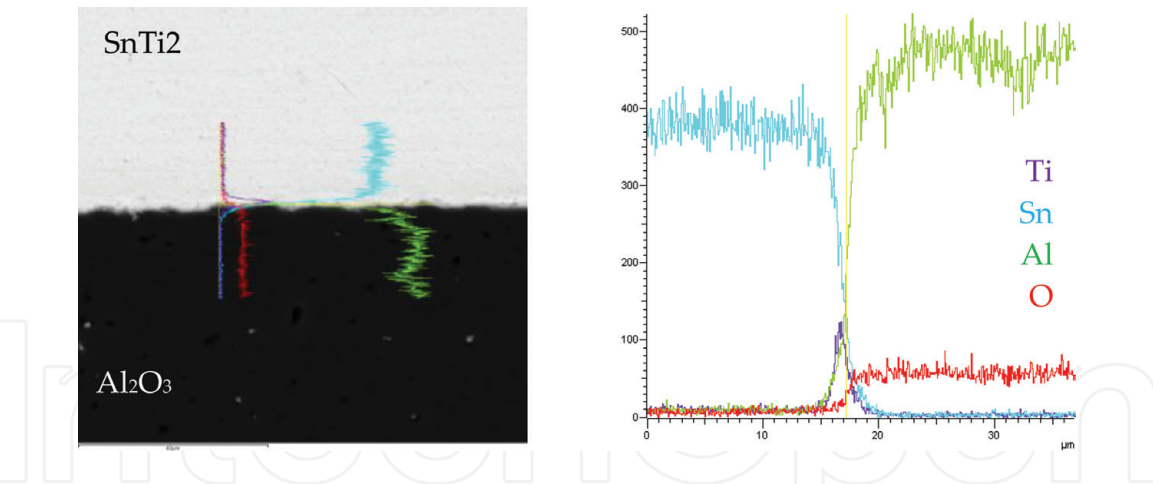*Microstructure of interface of Al_2O_3-$SnTi_2$ joint (SE).*

Figure 23.
Microstructure of interface of Al$_2$O$_3$-SnTi$_2$ joint (SEM) + concentration profiles of elements.
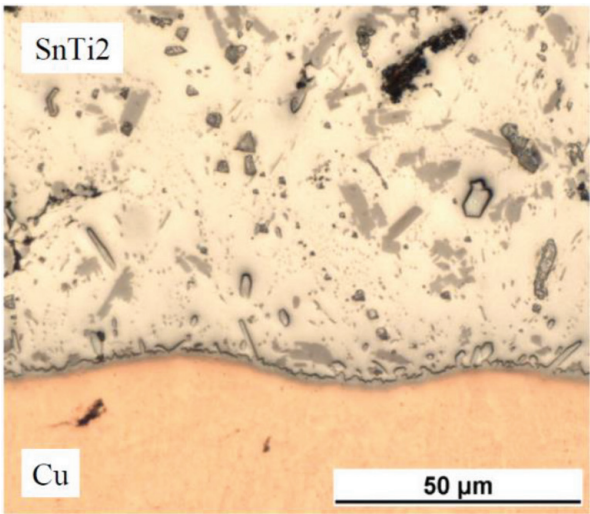

Figure 24.
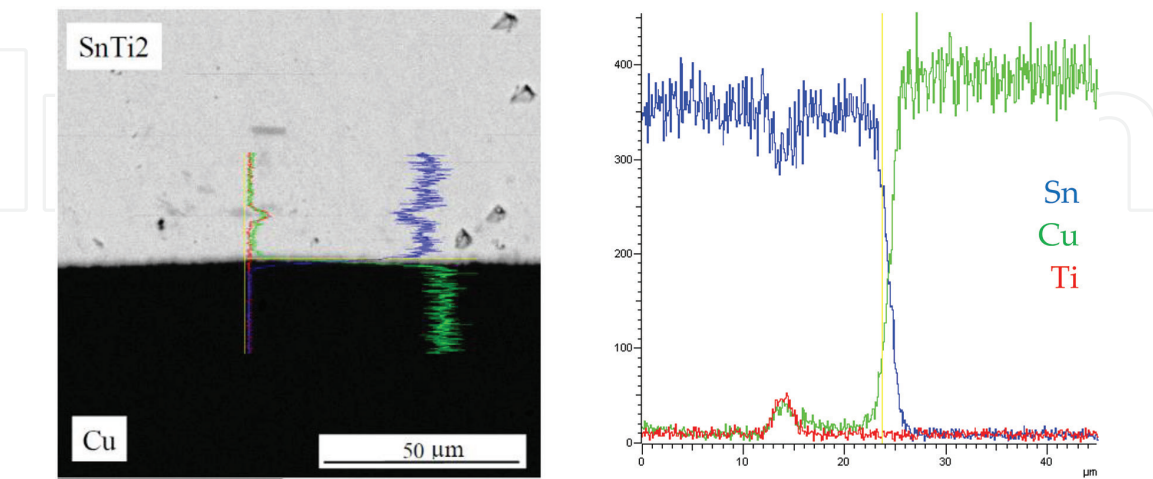*Microstructure of interface of Cu-SnTi$_2$ joint (SE).*

Figure 25.
Microstructure of interface of Cu-SnTi$_2$ joint (SEM) + concentration profiles of elements.

Sn matrix. We suppose the formation of similar Cu$_6$Sn$_5$ and Cu$_3$Sn phases as in the case of SnAg$_{3.5}$Ti$_4$(Ce,Ga) solder. The thickness of layer of intermetallic compounds depends on the level of soldering temperature and partially also on the dwell time at soldering temperature. Based on the records from EDW analyses, it may be

concluded that Ti does not contribute in bond formation, but it is locally bound in the dark phases contained in solder matrix (**Figure 25**).

4. Conclusions

The aim of this chapter was to study the soldering of metallic and ceramic materials by the lead-free active solders based on Sn and Bi. Possibility of soldering ceramic materials is in considerable measure limited by the poor wettability of ceramic substrates with commercial solders at classical soldering technologies and owing to different thermal expansivity of soldered materials. Solderability study includes the application and subsequent study of soldering technology with ultrasound assistance applicable for ceramic materials and design of solder which allows to fabricate qualitatively acceptable soldered joint. From amongst the numerous methods used at present for joining ceramic materials, the technology of soldering with active solders was selected. This technology allows to wet both the metallic and also non-metallic materials as glass, ceramics, silicon, composites, etc. The power ultrasound was selected for mechanical activation of solders. Wetting of hard-to-wet materials is achieved just by ultrasound application, since it generates the cavitation in the liquid solder which disrupts the surface oxides, changes the surface energy of ceramic materials and supports the diffusion processes in the interface. The solders and soldered joints were subjected to a wide scope of analyses and experiments. The microstructure of solders was assessed in an initial state. The phase composition of solders was identified by the diffraction analysis.

Also static shear test was ranked to the tests of technological solderability of soldered joints. A series of combined soldered joints of Cu/Al_2O_3, fabricated with $SnTi_2$, $SnAg_{3.5}Ti_4(Ce,Ga)$ and $BiIn_{25}Sn_{18}$ solders was assessed by the performed experiments. The interfaces of soldered joint were analysed by the optical and scanning microscopy and by the SEM technique with EDX microanalysis. By the gradual selection, based on the desired properties, the soldering alloy type $SnAg_{3.5}Ti_4(Ce,Ga)$ was finally identified as the most perspective solder. This solder exerts a narrow melting interval from 221.4 to 224.6°C. The attained tensile strength was 53 MPa, whereas the shear strength varies within the range from 29 to 45 MPa. Regarding the mechanism of bond formation, it was revealed that the joint between the $SnAg_{3.5}Ti_4(Ce,Ga)$ solder and substrate is created by the formation of a continuous reaction layer of Ti with the surface layers of Al_2O_3 ceramics.

Acknowledgements

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