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Recent Advances in Solderability of Ceramic and Metallic Materials with Application of Active Solders and Power Ultrasound

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Additional information is available at the end of the chapter

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Abstract

The Chapter deals with solderability of ceramic materials by ultrasound and suitable selection of soldering alloy. The solderability issue of ceramic materials consists mainly in the fact that the ceramic materials are not wettable by the common solders, due to their ionic and covalent bond between the atoms. However, there exist several ways to ensure the wettability of ceramic material surface. One of them is for example coating of ceramic material by a metallic layer. Anyway, a more perspective solution seems to be the application of soldering alloys which are alloyed with a small amount of alloying elements which exert high affinity to some component of ceramic material. The basic group of such solders are the so-called active solders containing from 1 to 5 wt. % Ti. Another group of solders, which may wet the ceramic material, are the solders alloyed with a small amount of lanthanides, for example La, Ce etc. The content of lanthanides varies from 0.5 up to 2 wt. %. The last group consists of the solders containing indium in the amount from 20 to 100 wt. %. The aim of study was to compare these three groups of soldering alloys from the viewpoint of mechanism of bond formation. The interactions between the solder and ceramic substrate were analysed and shear strength of fabricated soldered joint was determined. To improve the solderability, the soldering in combination with an active power ultrasound was also employed.

Keywords: solder, active solder, metallic materials, ceramic materials, ultrasonic soldering, wetting, shear strength, tin, indium, lanthanum, EDX analysis

1. Introduction

Creation of a sound bond of ceramic materials mutually or in combination with metal depends on the fact that whether a close contact to atomic distance is formed on the but surface and

whether ceramic material is wetted with the metallic solder. Wetting the ceramics with a metallic solder is an essential precondition for soldered joint formation.

Several ways may be used for ensuring the wettability of a ceramic material. For example, the deposition of solderable coating on ceramic material is often employed.

However, more modern methods seem to be the application of solders which are alloyed with some active metal such as Ti, In, Si, Al, Mg and/or lanthanides, which exert a strong chemical affinity to oxygen.

The first group comprises the active solders based on Sn or Sn-Ag, which may contain from 1.5 to 4 wt.% Ti. Another group of solders, which may wet the ceramic material, consists of solders alloyed with a small amount of lanthanides, for example, La, Ce and so on. The content of lanthanides usually varies from 0.5 to 2 wt.%. The last group are the solders containing indium in the amount from 20 to 100 wt.%. However, solving the mentioned issue still involves the requirement to ensure a joint that should resist the effects of residual stresses formed owing to different coefficients of thermal expansivity of metal and ceramics, which usually exerts much lower expansivity. This condition is most essential from the viewpoint of ensuring the reliability of ceramics/metal joints [1].

2. Methods of soldering ceramic materials

The biggest issue in the fabrication of joints of ceramic and non-metallic materials with metals consists in the fact that the commercial solders generally do not wet the ceramic materials. Poor wettability of ceramics is caused by the non-metallic character of bond, which is mostly ionic or covalent, in contrary to metallic materials with different structure of energy levels of electrons.

The following methods are mostly used to ensure the wettability:

- Metallizing of ceramics (e.g. metallic deposit of Mo-Mn paste, physical vapour deposition (PVD) and chemical vapour deposition (CVD) processes).
- Application of an active brazing alloy and/or solder alloyed with active elements (Ti, Zr, Hf).

All the mentioned technologies are applicable for soldering the ceramics/metal combinations. Regarding the versatility of technology, its ease and economic efficiency, there is increasing tendency to apply the soldering with an active solder. Soldering of metallized ceramics requires several additional operations, when compared to the application of active solders [2].

2.1. Soldering of metallized ceramics

Metallizing of ceramics eliminates the issues connected with its wettability. Regarding the selection of metallizing, it is necessary to know at what working temperature the soldered part will be servicing. Then, either solder and/or brazing alloy will be used. The desirable metallic layer may be obtained:

- By burning-in of metallic solution either of heat-resistant metals such as Mo, Mn, W or precious metals such as Ag, Au, Pt and so on.

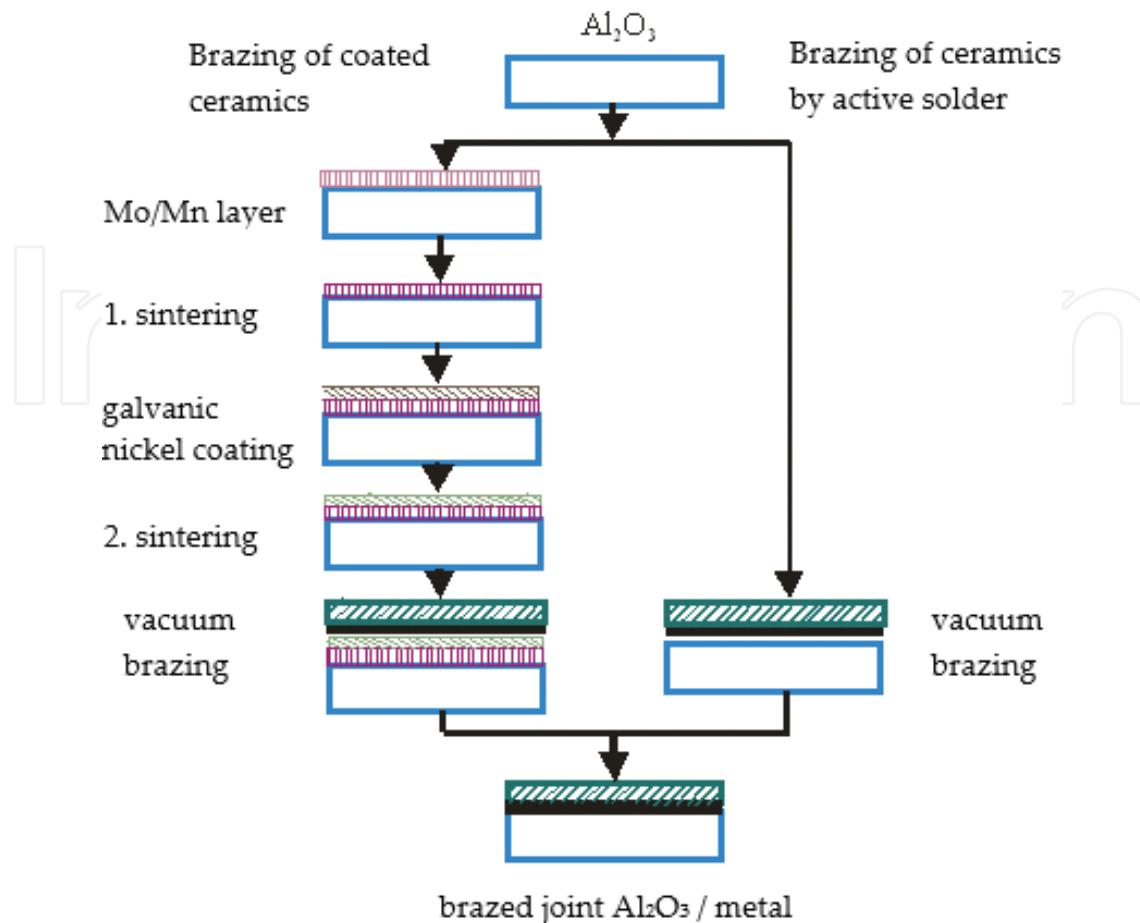


Figure 1. Schematic representation of vacuum brazing of metal and ceramics, metallized (with Ag72Cu brazing alloy) in comparison with non-metallized substrate (brazing with active Ag72CuTi brazing alloy) [3].

- By physical and chemical deposition, with a thin coatings, for example, of Au, Ag and Ni are created.

The classical method of metallizing Al_2O_3 ceramics is shown in **Figure 1**. A powder deposit (70% Mo, 17.5% Mn, 3.5% titanium hydride, 9% kaolin) is applied onto ceramics surface, followed by sintering at 1200–1400°C/10 min in humid hydrogen. If a silver brazing alloy (e.g. Ag72Cu) is used for brazing, then the sintered surface must be coated with nickel, to allow the brazing operation in vacuum. Optimum thickness of metallizing is 0.02 mm. Deviations from this value may affect the strength of soldered/brazed joint. The paste is deposited on the soldered surface by a brush and on/or by silk-screen printing. The layers formed by this process ensure at certain conditions a good reliability, however, paid by high power demands and necessity of costly equipment and extensive safety precautions at their preparation [4].

Chemical reactions between the Al_2O_3 substrate and molybdenum-manganese suspension allow joint formation. In case of this method, the reactions take place in the following manner:

- At sintering the metallic suspension with Mn in humid hydrogen, the manganese oxide is formed by the reaction [5]:



- The formed oxide then react with Al_2O_3 , forming thus the manganese-aluminium spinel as the product of reaction [5]:



2.2. Solderable metal coatings on ceramic materials formed by physical and chemical deposition

The methods for the formation of metallic layers and ceramic or glass substrates may be divided into several groups. The layers are obtained by chemical deposition from solutions of appropriate metal salts (e.g. Ni, Ag, etc.) by the aid of chemical agents, such as formaldehyde, hypophosphite, glucose and so on, with eventual heat treatment of the segregated coating. These layers are used in cases when small areas are metallized, eventually a motive composed of individual narrow conductive tracks, which are not mechanically loaded. Soldering of such layers requires the application of solders containing Sn, In, Cd and so on, with a low melting point (max. 200°C) and a minimum dwell time on soldering temperature [6].

Other known methods comprise the physical deposition by vacuum evaporation and sputtering of metallic layers as shown in **Figure 2**. These processes employ a high vacuum and temperatures within the range from 200 to 500°C . In case of these methods, the coating particles are deposited rather in physical manner, not by the aid of chemical reactions, as in the case of CVD (chemical vapour deposition) processes.

The thickness of evaporated or sputtered layers varies in the order of nm to μm . To prevent the de-alloying (de-wetting) of the metallic layer to the molten solder, the multiple deposition of system consisting of several metals, for example, Cr/Ni-Ag, Ni-Ag and Cr- Ni/V-Ag, is used.

To ensure a good spreadability of solder over the entire surface, the final layer is often formed by evaporation or sputtering of Au or Ag, which is dissolved in the used solder and will thus create suitable conditions for a good wettability of entire surface by the solder. Chemical reaction of the deposited layer with the material of ceramic substrate does not occur in both mentioned deposition methods. The bond between the layer and ceramics is mostly of adhesion character [2]. The solderable coatings for ensuring the wettability of poorly wettable surfaces are mostly employed in the electrotechnics and electronics. The advantage of well-solderable metal coatings consists in the fact that the soldering process can be accomplished in very short soldering times. The used coatings are either meltable or soluble (**Figure 3**). The soluble

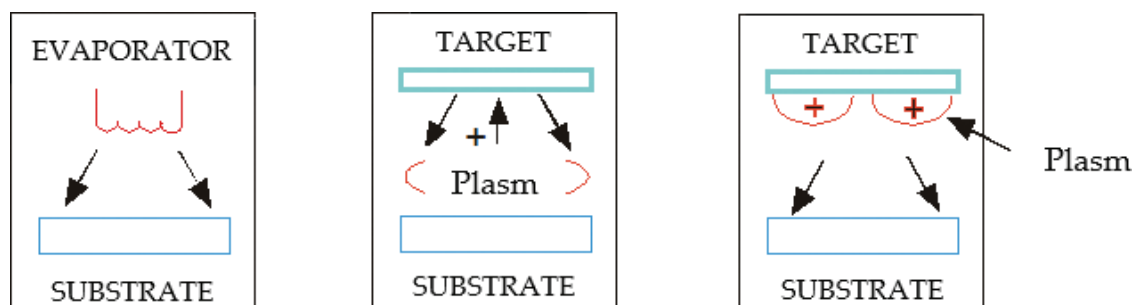


Figure 2. Main physical deposition methods applied for metallizing of ceramics [7]: a, evaporation; b, diode sputtering; c, magnetron sputtering.

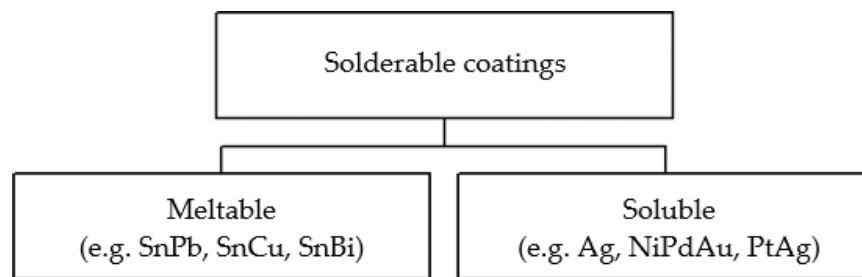


Figure 3. Basic division of solderable coatings [7].

coating may consist of one metal or of several metal layers deposited subsequently on the substrate. The melttable coating is formed by the deposition of the lead- and/or lead-free layer of soldering alloy on the substrate surface.

The system of dissolvable solderable coating in electronics mostly consists of an adhesion layer (Cr, Ni, Ti, Al), a diffusion barrier (Ni, Cr) and a solderable layer (Ag, Au, Cu, Ni), whereas its composition depends on the substrate material and parameters and conditions of soldering. For preserving a good solderability, for example tinning with pure tin, metallizing with Sn-Pb solders, gold and/or silver plating used to be applied until now. However, the application of lead-free soldering necessitates the new approaches also in the field of surface finishing, especially in printed circuits and also outlets of electronic components. The melttable coatings must be selected without lead content, regarding thus the environmental viewpoint. The coatings composed of SnBi and SnCu, eventually coating of pure tin, start to be more favourable nowadays [8].

A coating composed of a system of Cr/Ni-7%V/Ag layers, prepared by PVD sputtering, was approved experimentally. The chromium layer has the adhesion function, Ni-V is the diffusion barrier and Ag layer ensures a good wettability and spreadability in a short time as shown in **Figure 4** [8].

The SnIn52 solder with a melting point of 120°C was proposed for soldering. The soldering temperature was selected just by 10°C higher than its melting point with a minimum dwell time, needed for a proper spreading of the solder.

2.3. Soldering of ceramic materials with an active solder

The wettability of ceramic material may be improved by reducing the interphase stress on the ceramics/substrate interface, by solder alloyed with an active element (mainly Ti, Zr or Hf is mostly mentioned in the literature) with a high affinity to oxygen, which reacts with ceramics during the soldering process, whereby bonds on the interatomic level are formed. The basic chemical reaction between Ti and oxidic ceramics has a general form [16]:

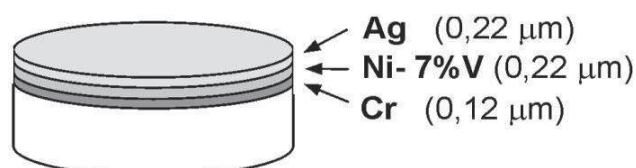


Figure 4. Distribution of metallic layers on a substrate [8].



Titanium can bond considerable amount of oxygen in ceramics of oxidic type. Therefore, several oxides can be formed, for example, between the AgCuTi solder and Al₂O₃ ceramics: TiO, Ti₂O₃, Ti₃O₅, Ti₄O₇ and TiO₂. The reaction product formed on the contact area at individual types of oxidic and non-oxidic ceramics is several μm in thickness and depends on the soldering conditions and solder type. The reaction product alters the surface energy of ceramics and allows its wetting by the solder [17]. Higher concentration of active element may in some cases increase the joint brittleness; therefore, its amount must be limited. The foreign sources refer the maximum limit to 4 wt. % Ti in an eutectic solder-type Ag72Cu. Chemical changes occurring on the ceramics-active solder interface are very complex since the concentration gradients are formed [1].

The process of soldering ceramics with metal is significantly simplified by the application of active solders. Soldering ceramics with an active solder is also more economically efficient, since the multi-stage metallizing processes with demanding inter-operational annealing are unnecessary [9].

2.4. Division of active solders

The active solders, similar as the commercial solders, are classified by the melting temperature to solders, brazing alloys and high-temperature solders. The difference is seen just in the case of active solders, which may be further divided into high-temperature solders and the mechanically activated solders. Due to reaction capability of an active element, the soldering temperature for high-temperature activated active solders must be higher than 780°C (at the application of active Ti). Nevertheless, the active solders are molten at the temperature around 220°C. The division of active solders and their chemical base is given in **Table 1**.

2.5. Active solders

The brittle materials as vitreous glass (SiO₂), silicon, graphite and so on can be soldered with active solders. Base metal of active solders is mostly tin, lead or indium and the alloys created

Active solders	Application temperature	Chemical composition
Active solders	From cryogenic temperatures up to about 150°C	Sn, In and Pb based, for high-temperature activation (e.g. Sn95Ag5Ti3)
		Sn and In based, for mechanical activation (e.g. SnAg6Ti4Ce)
Active brazing alloys	up to 350°C	Ag, Cu and Au based (Ag72CuTi1,5)
High-temperature active solders	up to 900°C	Ni, Co, Pd and Pt based (e.g. Ni70Hf30)

Table 1. Division of active solders by the melting temperature [10].

on their basis. However, the lead-containing solders are not suitable for soldering in vacuum, since considerable evaporation of lead and also furnace contamination occurs. When soldering with lead, a through-flow atmosphere with pure argon, eventually helium with overpressure attaining 0.1–0.2 MPa, should be used [11].

The solders used in joint assembly are capable to compensate the stresses resulting from different thermal expansivity, owing to their plastic straining by the shear or creep mechanism. In this way, the most significant reduction of residual stresses at preserved joint simplicity may be achieved. The presence of an active element ensures a good wettability of soldered parts.

The active solders can be used for soldering unusual combinations of metallic materials (e.g. CrNi steel, Mo, W, Ti, Cr, etc.) and non-metallic materials, mostly of brittle character (vitreous glass, sapphire, carbon, silicon and also almost all types of ceramics) [11]. Such joints are applied mainly in electronics and electrotechnics, where lower strength and thermal resistance of the joint are sufficient. For example, the soldering of glass in lasers and spectrometers, creation of electric connections with graphite, connecting the heat exchangers to ceramic electronic substrate of Al_2O_3 , or AlN [12]. The solders also allow fabricating the vacuum-tight joints in vacuum and cryogenic technology, where the application of indium-based solder was well approved [11].

Great attention is paid to issues of soldering with active solders, especially for the electronic applications. However, there are still many issues, regarding the achievement of the desired utility properties of joints, to be solved.

As already mentioned, the active solders may be further divided according to the way of active element activation in the solder to the solders destined for:

- high-temperature activation,
- mechanical activation.

The active brazing alloys for high-temperature activation based on Ag and Ag-Cu, designated as CB 2, CB 4, CB 5 and CB 6, are supplied by Umicore-BrazeTec GmbH, Germany. The brazing alloy designated as CB 10, with composition AgCu25Ti10, and the alloy designated as CB 11, with composition AgTi10, are supplied in the form of brazing paste. The working temperature of these brazing alloys is 850–1050°C. The solders for ultrasonic activation, designated as CERASOLZER, are supplied by the Japanese company KURODA ELECTRIC.

The solders for mechanical (ultrasonic) activation, designated as S-Bond, are supplied by the Euromat, GmbH, Germany. It concerns, for example, the solders type S-bond 140 (based on Bi-Sn-Ag-Ti), S-bond 220 (based on Sn-Ag-Ti), S-bond 400 (based on Zn-Al-Ag) and so on. The soldering temperature for the S-bond 140 solder is from 150 to 160°C, for the S-bond 220 solder it is 240–260°C and for the S-bond 400 solder the soldering temperature is 420–430°C. It was proved experimentally, that the S-bond 220 (SnAg6Ti4Ce) solder has wetted the Al_2O_3 ceramics with the wetting angle of 62°, when applied at a temperature of 860°C in vacuum of 10^{-2} Pa. This experiment was performed in cooperation with the Institute of Materials and Machine Mechanics at the Slovak Academy of Sciences in Bratislava.

2.6. High-temperature activation

It is a process being performed at high temperature (850–950°C), mostly in vacuum furnace with the shielding atmosphere of argon as shown in **Figure 5**. It was found out experimentally that at activation with Ti-active element, the lowest temperature at which wetting of Al_2O_3 ceramics may be achieved is 780°C. However, wetting depends also on the content of Ti-active element in the solder [7].

With increasing soldering temperature (activation temperature), the wetting of ceramic material is enhanced by high-temperature activation but, in contrary, if a ceramic material is soldered in combination with metallic material, the degradation of base metal by erosion may occur.

2.7. Mechanical activation

The mechanically activated solders allow wetting the metallic and non-metallic materials at considerably lower temperature than in the case of high-temperature activation. Moreover, there is no need to solder in vacuum and/or in the shielding atmosphere. In dependence on soldering alloy type, this temperature may vary from 150 to 430°C, thus in the temperature range of soldering with solders, which are based on Bi-Sn, Sn-Ag or Zn-Al, as already mentioned. This unique capability is allowed by a slight addition of the following metals: lanthanum, cerium, yttrium and samarium (lanthanides), which occur in the soldering alloy matrix. These metals at the same time create a protective barrier for the active metal (Ti) as shown in **Figure 6** [13]. Mechanical activation can be performed by

- intrusions
- vibrations (50–60 Hz)
- ultrasound (20 60 kHz)
- friction (different processes)—**Figure 7**.

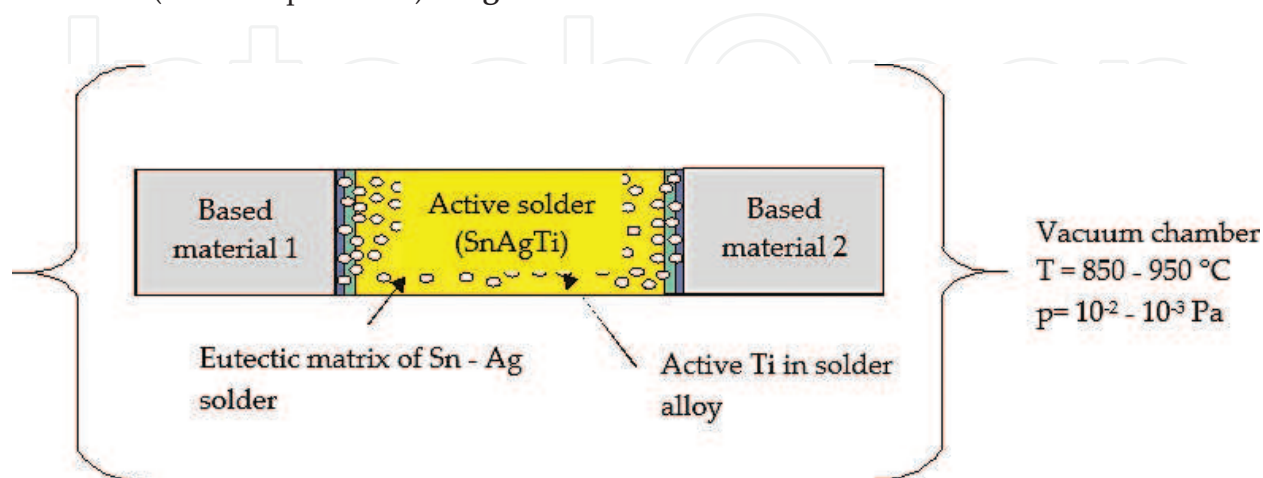


Figure 5. Scheme of soldering with high-temperature activation in vacuum [14].

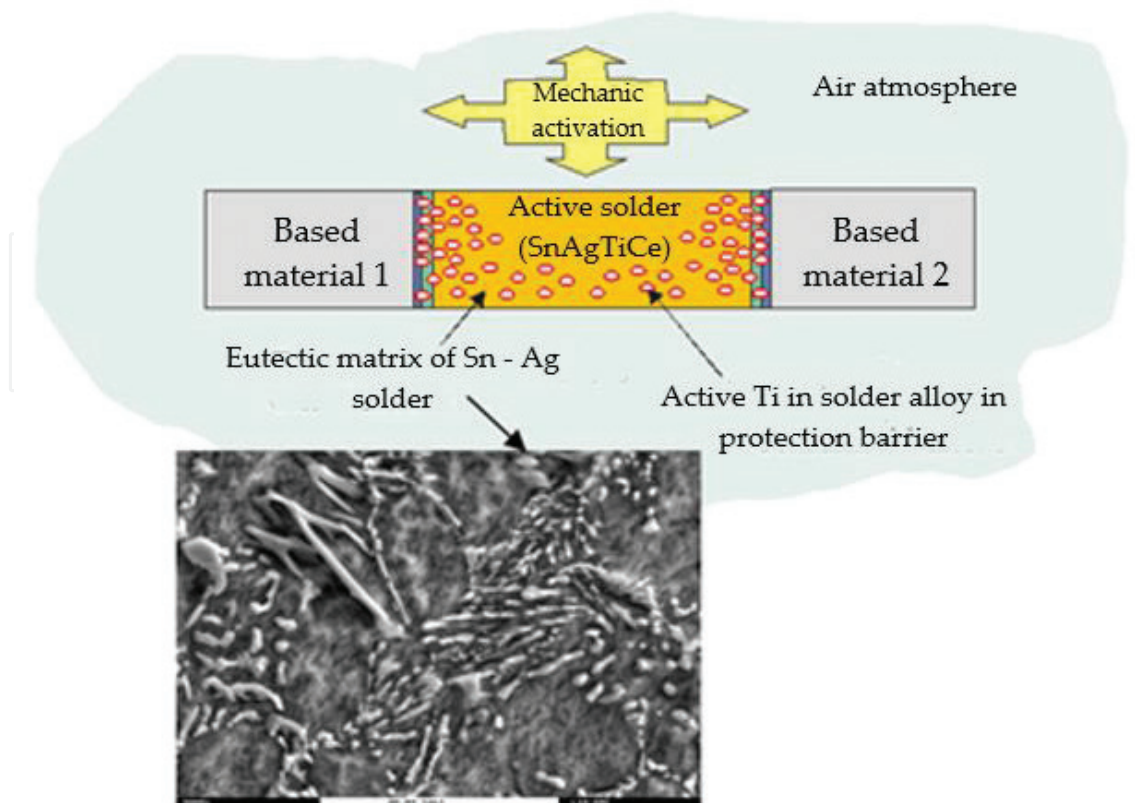


Figure 6. Scheme of soldering with mechanical activation in air without flux—S-Bond process [14].

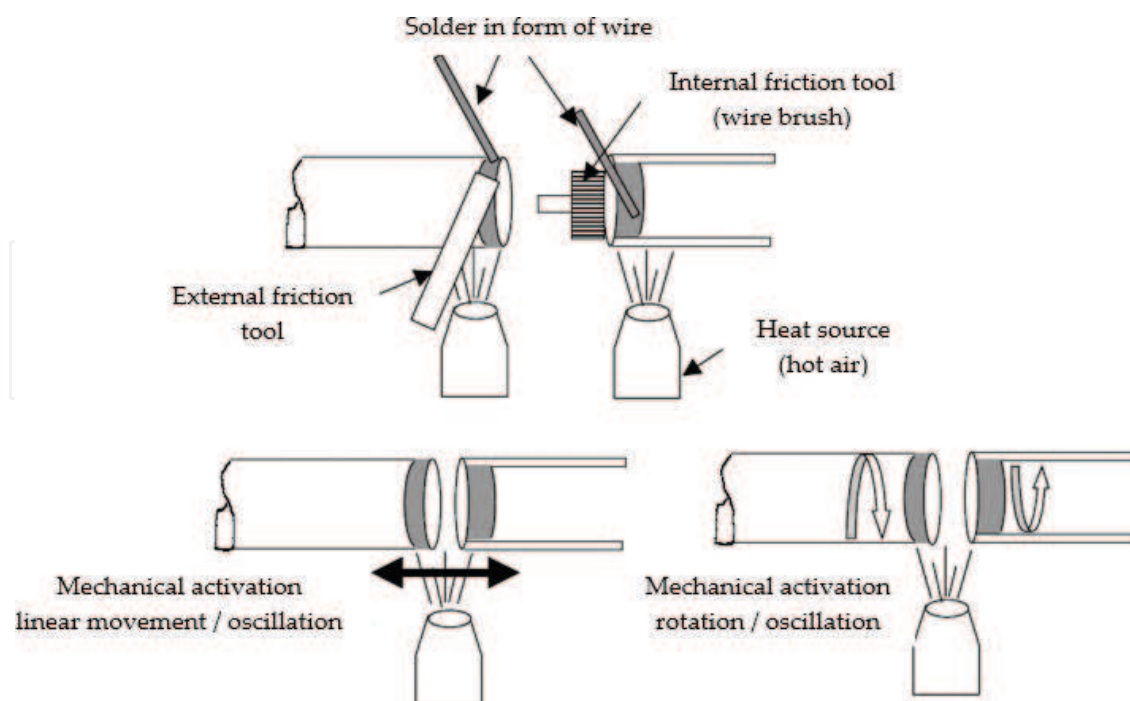


Figure 7. Scheme of different ways of mechanical activation of solder by friction [14].

2.8. Wetting

The wettability is qualitatively assessed by the wetting angle Θ and adhesion work W_{ad} [15]. It is defined as the capability of molten solder to adhere to a clean surface of material joined at a certain temperature [16]. Wetting of surfaces is at the same time the primary precondition for joint formation. Wetting is realized either by Van der Waals bond and/or by chemical bonding. Thus, two basic types of wetting may be distinguished [15]:

- Wetting without chemical reaction in the soldered material-solder interface.
- Wetting, where chemical reaction in the solder-soldered material interface takes place, whereby also the formation of reaction products (new phases) occurs.

The equations describing wetting of liquid droplet on a solid material surface were derived on the basis of physical and chemical principles. The droplet during wetting takes such a shape, at which the energy of solder-material-atmosphere (vacuum) system is minimum, and thus the interatomic forces may be exerted [16]. The basic Young's equation for a weak reaction system may then result from the facts mentioned [17]:

$$\gamma_{SV} - \gamma_{SL} = \gamma_{LV} \cos \Theta \tag{4}$$

where γ_{SV} is the surface energy between the material surface and atmosphere, γ_{SL} is the surface energy between the material surface and solder, γ_{LV} is the surface energy between the solder and atmosphere and Θ is the wetting angle.

The magnitude of wetting angle is the qualitative criterion of wetting. **Figure 8** shows two basic cases which may occur at material wetting with a liquid solder.

As obvious from **Figure 8**, the solder does not wet the material for which the value of wetting angle $\Theta > 90^\circ$ ($\gamma_{SL} < \gamma_{SV}$). If the value $\Theta < 90^\circ$, the solder wets the material. By the equation of wetting (4), the driving force of process is the ($\gamma_{SV} < \gamma_{SL}$) difference. By the magnitude of wetting angle, we distinguish different degrees of wetting—**Table 2** [16].

Lowering the contact angle of wetting and increasing the value of adhesive work at a defined solid substrate may be affected by the selection of a suitable solder. However, for wetting

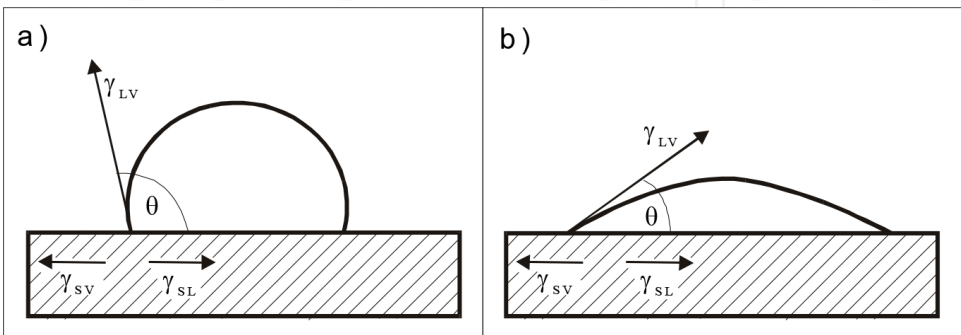


Figure 8. Scheme of wetting for a weak reaction system. (a) Solder does not wet the material; (b) solder wets the material.

Wetting degrees	Contact angle
Excellent (full)	$\Theta = 0^\circ$
Very good	$\Theta < 20^\circ$
Good	$20^\circ < \Theta < 90^\circ$
Poor	$\Theta > 90^\circ$

Table 2. Assessment of wetting.

ceramic materials, it is necessary to use an active solder, that is, the solder containing the element chemically active towards ceramics (Ti, Zr or Hf). Such an element is chemically bond with some component of ceramics, so improving its wettability and thus also the joint strength [15]. Scheme of wetting for the system with reaction on the interface is shown in **Figure 9**. In such a case, Young's equation according to Ref. [18] attains the following form:

$$[\gamma_{SV} - (\gamma_{RL} + \gamma_{SR} + \Delta G \cdot t / \Omega)] = \gamma_{LV} \cdot \cos \Theta \quad (5)$$

where γ_{SV} is the surface energy between the material surface and atmosphere, γ_{LV} is the surface energy between the solder and atmosphere, γ_{RL} is the surface energy between the solder and reaction layer, γ_{SR} is the surface energy between the reaction layer and material, Θ is the wetting angle, Ω is the gram atomic volume, t is the thickness of reaction layer and ΔG is the change in free energy per one mole of reaction product.

2.9. Compensation of different thermal expansivity of the ceramics/metal-soldered joints

The residual stresses in soldered joint of two materials with different coefficients of thermal expansivity belong to one of the most serious issues for ensuring the reliable joints of ceramics/metal. Ceramic materials exert in general lower coefficients of thermal expansivity and are not capable of plastic strain. On the contrary, the metals exert much higher coefficients of thermal expansivity and are in certain extent capable of plastic strain. These are the main reasons for the formation of residual stressed during cooling down of ceramics/metal joints, which must be compensated.

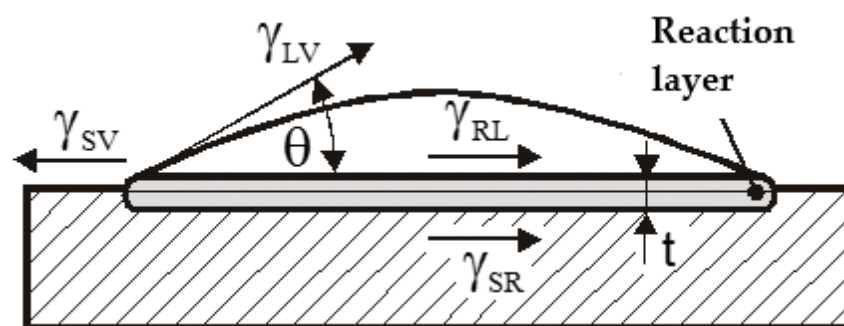


Figure 9. Scheme of wetting for the system with reaction on the interface [18].

Reducing the level of residual stresses may be more or less attained in the following ways [7]:

- *By the selection of suitable material couples.* Application of joined materials with similar coefficients of thermal expansivity is not a practical solution in most cases, since the joined materials are mostly selected on the basis of other desired properties and not on the basis of their thermal expansivity.
- *Soldering temperature.* By selection of a suitable solder (regarding thermal resistance of the joint), reduced soldering temperature may be achieved.
- *Shape of joint and thickness of the materials joined.* A simple type of joint should be selected, attaining thus the compressive loading in ceramic material. It should be taken into account that the ceramic materials do not exert constant value of strength limit. This is in practice exerted in such a way that during loading of ceramics a crack may be formed without any strain.
- *Size of clearance between the soldered parts.* In soldering-combined materials, it is required that the joint clearance should be generally greater than in the case when soldering the same materials (**Figure 10**). It is recommended to select the clearance value within $s = 0.2\text{--}0.5\text{ mm}$ [19].
- *Application of interlayer.* If allowed by the design solution of the joint, the reduction of residual stresses can be attained also by the application of an interlayer, where material is selected on the basis of elastic, plastic and thermal properties. At the application of interlayer with a small coefficient of thermal expansivity, close to that of ceramics (W, Mo), lower stresses are formed in the ceramics. In the case of application of interlayer with a low yield point (Ni, Cu, Al), the level of stresses is reduced due to their relaxation by the slip mechanism. At the application of a composite interlayer (e.g. cermet-sintered interlayer composed of ceramic and metallic powders) with gradual transition from metal expansivity to expansivity of ceramics, the creation of gradient of physical properties is considered as shown in **Figure 11**. In interlayer selection, it is also necessary to consider the interactions with the molten solder: segregation, formation of brittle structures on the interface and dilution in the solder.
- *Application of solder.* At the application of metal solders in the joint assembly, these are capable to compensate the stresses resulting from different thermal expansivity by their plastic straining via the slip or creep mechanism. In this way, the most significant reduction of residual stresses at preserved joint simplicity may be attained [2].

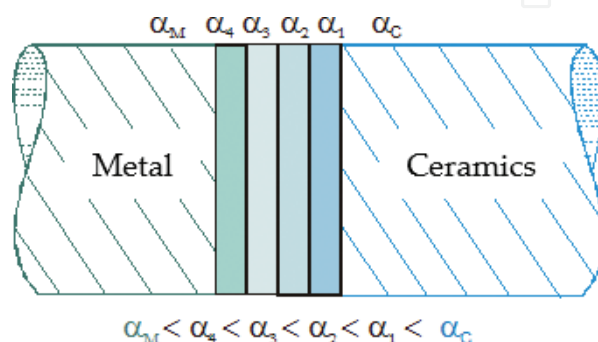


Figure 10. Complex interlayer [20].

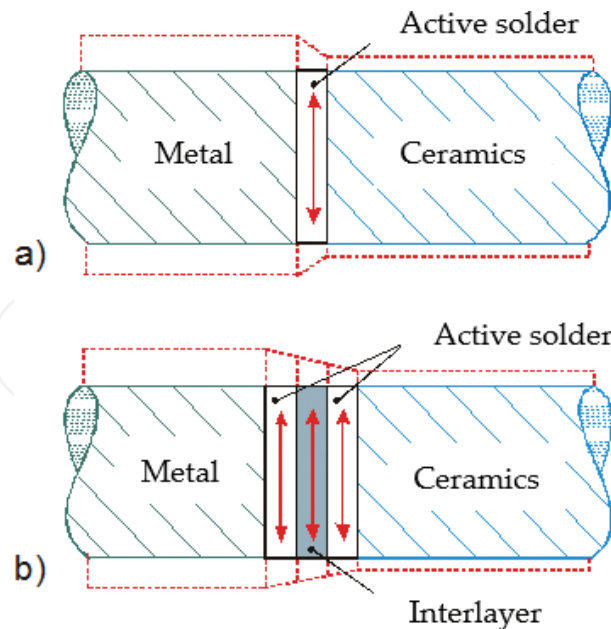


Figure 11. Reduction of residual stresses in contact zone by application of plastic metallic interlayer: a, joint without interlayer; b, joint with interlayer [21].

2.10. Indium-based solders

The indium-based solders, for example, type 100In or the solders type In-Sn with a higher indium content, are characteristic with their unique soldering properties. These solders allow to wet a wide range of metallic, non-metallic and ceramic materials, for example non-metallics such as glass, glazed ceramics, mica, mullite, quartz, fibre optic glass, lead glass, liquid crystal glass, metallized glass, optical glass, pyrex, quartz glass, sapphire, silica, silica glass, soda lime glass, and various metallic oxides [22]. During soldering process performed with high-indium solders in air, the indium suboxides are formed, which react with the surface oxides on the soldered substrate at the formation of a strong bond between the substrate and solder. An example of soldering the ITO ceramics ($\text{In}_2\text{O}_3/\text{SnO}_2$) presents the study [23], which deals with the application of soldering alloy type Sn-In-Ag-Ti at ultrasonic soldering of ITO ceramics. It was found that the Sn-In-Ag-Ti solder reacts with the surface of ITO substrate, whereby the wettability of materials joined and bond formation was ensured.

The goal of the next research within the study [24] consisted of soldering metallic (Cu, Ni, Al, Ti, AISI 316 steel) and ceramic materials (Al_2O_3 , SiC) by the aid of solders with a high content of indium at power ultrasound application. The solders with composition 100In (5N purity) and 70In30Sn (4N5 purity) were used in experiments. The UT equipment with a frequency of 40 kHz and an output power of 400 W with 2 μm amplitude was used for experiments. The scheme and description of this equipment is shown in **Figure 12**. Soldering temperature was 20°C above the liquidus of the solder tested. The dwell time at soldering temperature was 30 s and the time of ultrasound action on the soldered joint was 5 s. Heating of specimens was ensured by the hot-plate method with temperature control via a thermocouple type NiCr/NiSi. The shear strength of metallic and ceramic substrates was assessed. The test specimens of substrates were prepared in the form of disks with a diameter of Ø 15 mm and

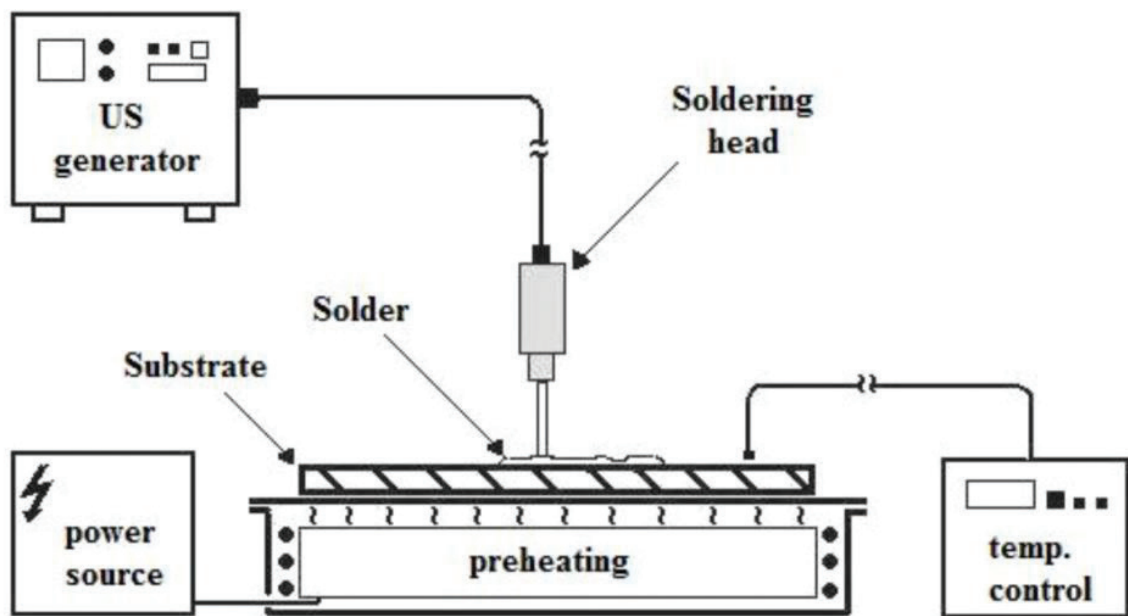


Figure 12. Scheme of ultrasonic device used for soldering.

1.5–2 mm in thickness. The test specimen is shown in **Figure 13**. The procedure of specimen preparation is shown in **Figure 14**. The shear gap was selected to 0.1 mm, which corresponds to 2% from the sheared diameter of the roll formed of the solder. Uniform testing rate was 0.5 mm/min.

The 100In and 70In30Sn solders with a high indium content wetted all studied metallic (Cu, Al, Ni, Ti and AISI 316 steel) and ceramic materials (SiC and Al_2O_3) at the application of power ultrasound with the frequency of 40 kHz. For comparison, the 100Sn solder wetted all metallic materials but it did not wet the ceramic materials in spite of ultrasound assistance. The 100Sn solder cannot be used for soldering ceramic and non-metallic materials.

The results of mechanical tests of soldered joints fabricated by the use of 100In solder are given in **Figure 15**. The highest shear strength of 12.5–54 MPa is achieved at the soldering of metals. The lowest shear strength was observed with aluminium and the highest with copper. Considerably lower shear strength values are achieved at the application of 100In solder on the ceramic materials, varying from 3.5 to 6 MPa. Higher strength was attained with Al_2O_3 ceramics and lower with SiC ceramics.

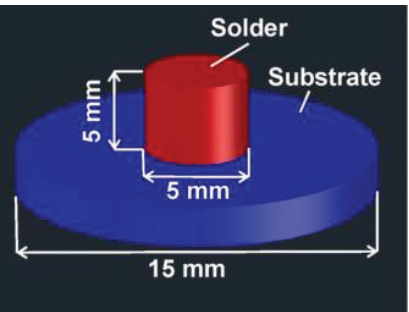


Figure 13. Fabricated test specimen.

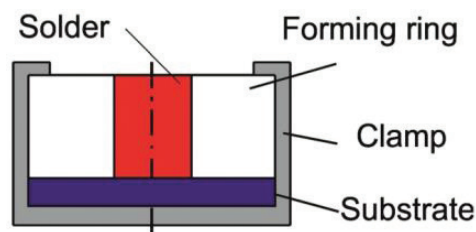


Figure 14. Specimen layout at its preparation for the shear test.

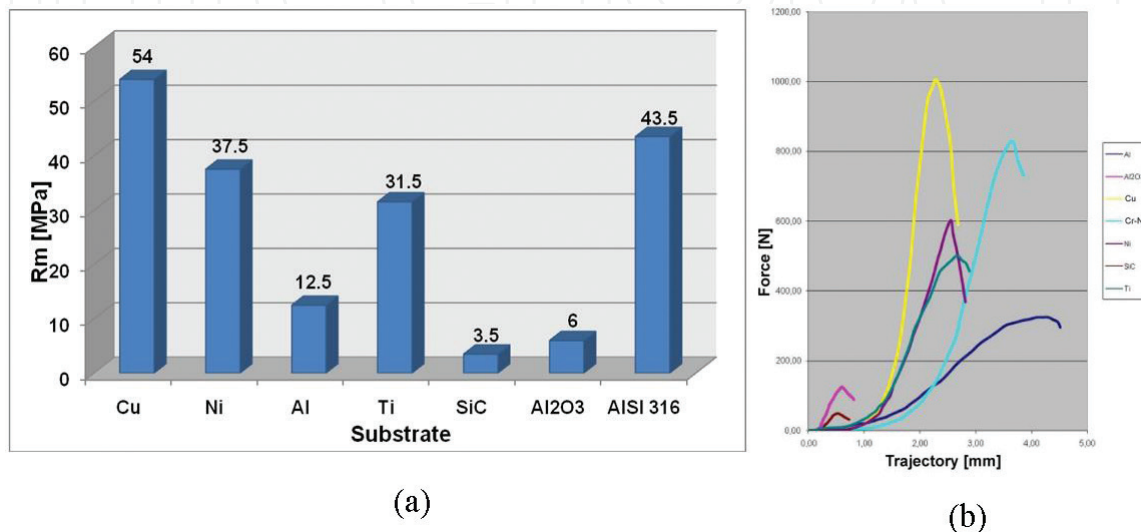


Figure 15. Shear strength of joints fabricated with solder type 100In.

At comparison of the results of shear strength attained with 100In and 70In30Sn solders (Figure 16), it was found that with the solder containing tin higher strength values are achieved, both on the metallic and ceramic materials. This is caused by the fact that the matrix of 70In30Sn solder exerts the eutectic structure [25, 26]; therefore, it offers also higher mechanical resistance, when compared to pure indium solder. At the In content of 70 wt. %, the solder preserves also suitable wetting properties and sufficient interaction with the surface of ceramic material. The shear strength achieved on metallic materials ranged from 23 to 71.5 MPa. It was the highest on copper and lowest again on Al. On the ceramic materials, it was 6 and 7 MPa as shown in Figure 16.

The fractured surfaces on metallic materials remained always covered with a uniform layer of solder after shear test. In case of ceramic materials, the fractured surface remained covered with a solder layer in most cases. Partial separation of solder from the ceramic substrate was observed approximately with 40% of all specimens. The fracture mostly initiated in the solder and was of ductile character. The failure took place in shear mechanism (Figure 17). The motion of shearing tool is clearly visible on the fracture morphology.

2.11. Active solder with lanthanum content

The research [27] was aimed at direct soldering Al₂O₃ ceramics with a copper substrate by the application of Sn2La solder. It was studied whether the Sn-based solder alloyed with La

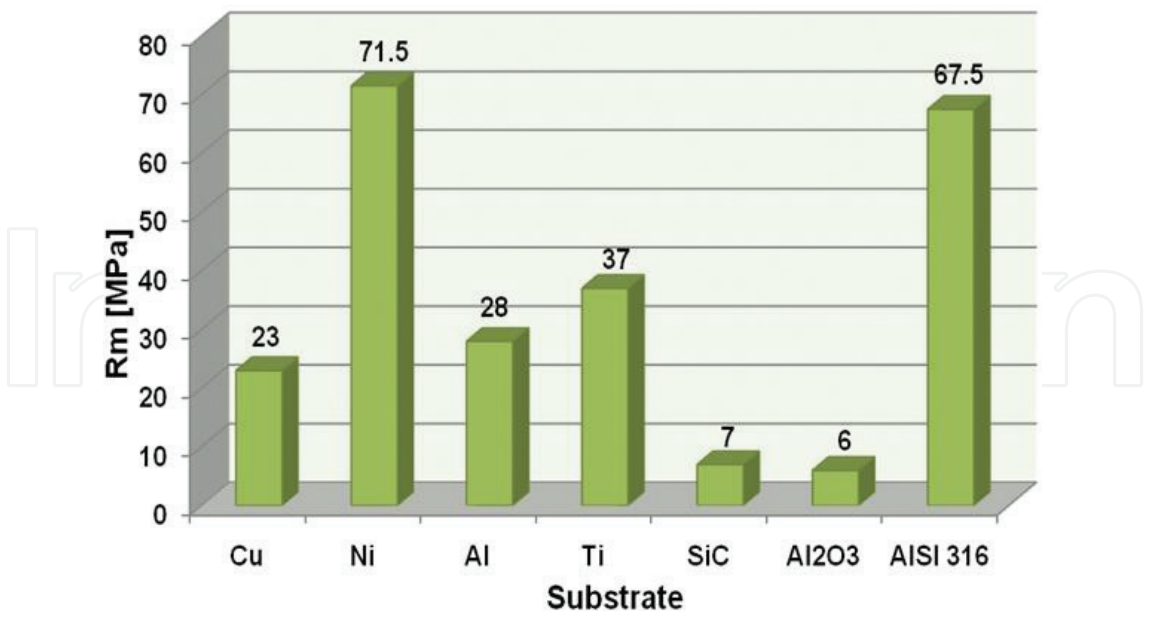


Figure 16. Shear strength of joints fabricated with solder type In70Sn30.

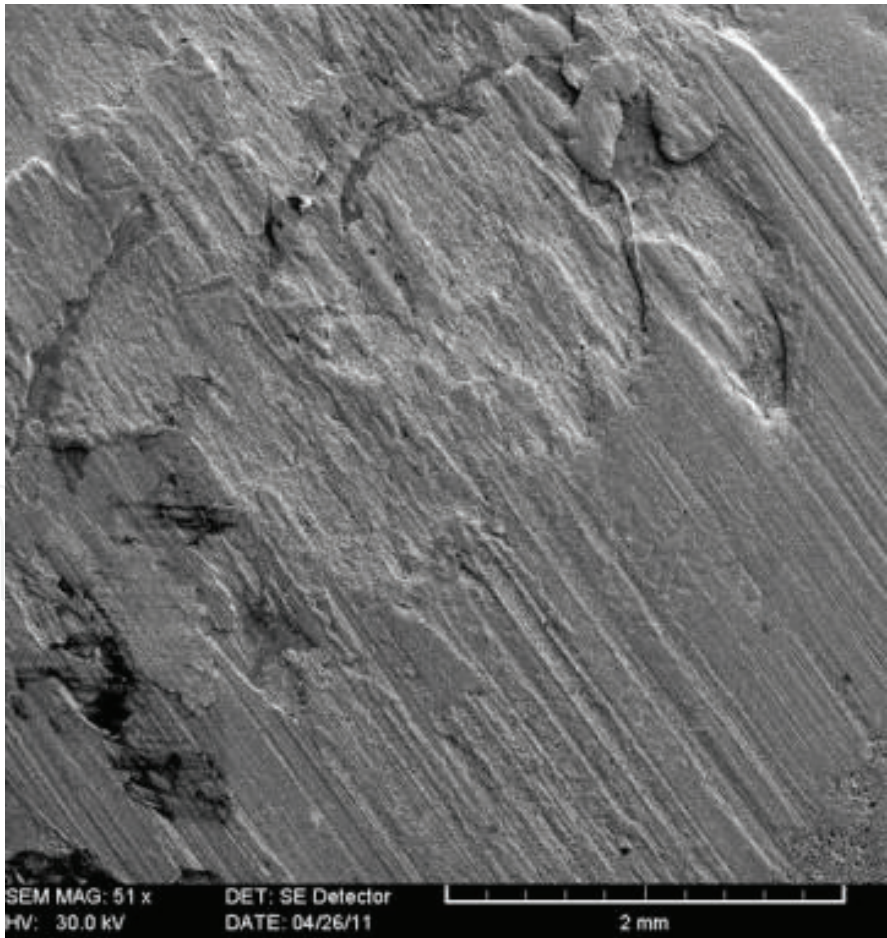


Figure 17. Fracture area of joint on the substrate of Al₂O₃.

can wet the Al_2O_3 ceramics and create thus a strong bond. The possibility to substitute La with Ti in active tin solders was also studied. For this reason, the analyses for revealing the mechanism of bond formation were performed, and the shear strength of the joints was measured. Lanthanum, as a metal with high affinity to oxygen, was applied as an active element. Soldering was performed at a low temperature in air with the application of power ultrasound. The ultrasonic equipment type Hanuz UT2 with the parameters given in **Table 3** was employed for soldering. An ultrasonic transducer was used for solder activation, which uses an oscillating piezoelectric system and a titanium tool with an outlet diameter of $\varnothing 3\text{ mm}$. The scheme of soldering with ultrasound assistance is documented in **Figure 18**. Soldering takes place through the layer of molten solder. The titanium tool, sonotrode, is thus not in a direct contact with the ceramic substrate. The soldering temperature was selected to 290°C , which is 20°C above the liquidus temperature of the solder.

Soldering procedure runs in such a manner that a layer of solder is deposited on the substrate heated at soldering temperature. The liquid solder is then subjected to active ultrasound without the application of shielding atmosphere, thus in air during the time of 5 s. After ultrasonic activation, the redundant layer of molten solder and formed oxides are removed from the substrate surface. Both substrates are prepared in the same way. The substrates with the deposited solder layer are put on each other in such a manner to create contact with the molten phase. They are then centred and the desired joint is formed by a slight compression of this assembly. Graphical representation of this procedure is shown in **Figure 19**.

Ultrasound power	[W]	400
Working frequency	[kHz]	40
Amplitude	[μm]	2
Soldering temperature	[$^\circ\text{C}$]	290
Time of UT activation	[s]	5

Table 3. Parameters and conditions of soldering.

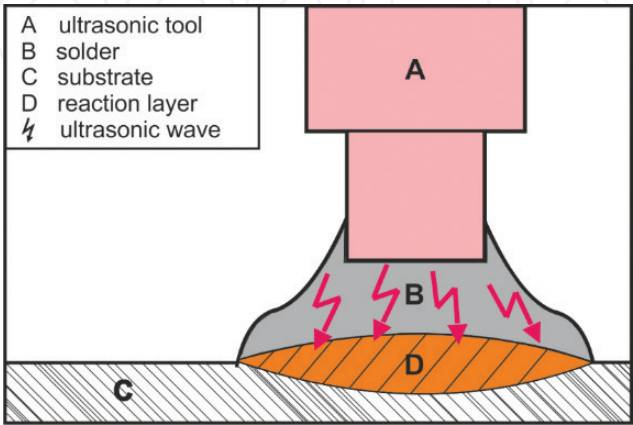


Figure 18. Ultrasonic soldering.

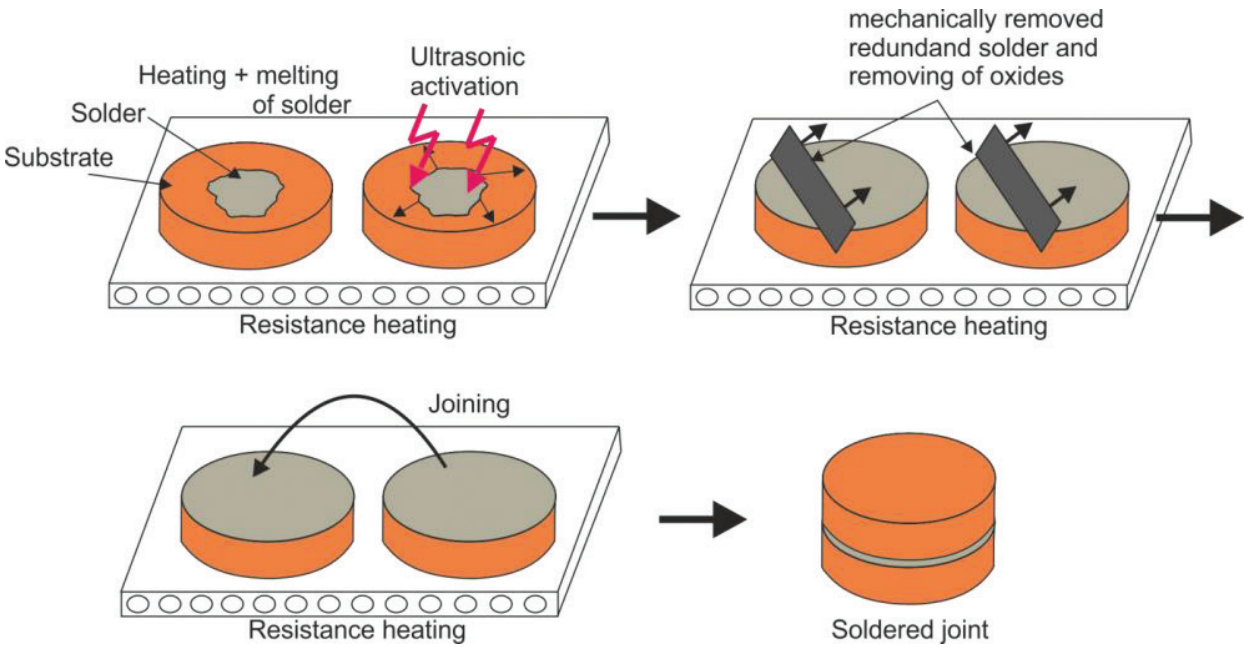


Figure 19. Procedure of joint fabrication by ultrasonic soldering.

A uniform distribution of La phases in tin matrix may be seen in the microstructure of Sn2La solder shown in **Figure 20**. No La was observed in the matrix of the studied solder. This fact was verified by the energy dispersive spectroscopy (EDS) analysis.

2.12. Analysis of interface in Al₂O₃/Sn2La solder joint

Comparison of microstructures of Al₂O₃/SiC and Cu/Cu-soldered joints from the optical microscopy is shown in **Figure 21**.

As shown, much of lanthanum is oxidized in air during ultrasonic process. The lanthanum particles are distributed to the interface with ceramic material during ultrasonic activation as shown in **Figures 22** and **23**, and they are then combined with oxides on the surface of ceramic material. The concentration line of La in **Figure 22** proves increased La concentration on the

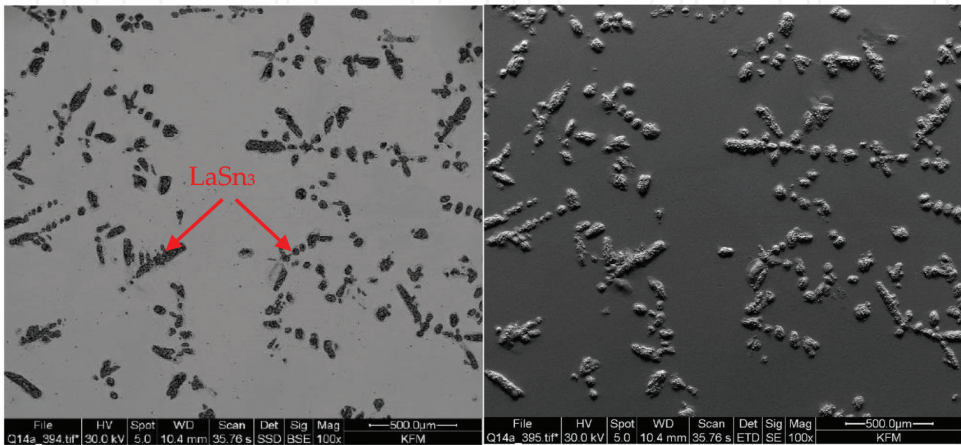


Figure 20. Microstructure of Sn2La solder.

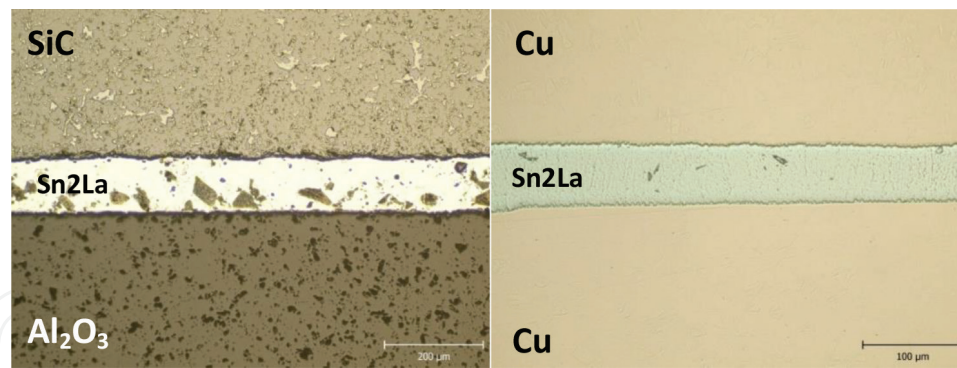


Figure 21. Comparing the microstructure of Sn2La solder after UT soldering at the same *parameters and conditions of soldering*.

interface with Al_2O_3 ceramics. A uniform, continuous layer of La oxides on the interface with ceramic material can be seen in **Figure 23**, which ensures the bond formation. The thickness of this layer is around $1.5\ \mu\text{m}$. In spite of this layer, the solder is more or less bonded to the ceramic substrate. The bond with ceramic material is of adhesion character. The formation of new intermetallic phases was not observed. This also causes lower shear strength of the bond with ceramic materials. The mechanism of bond formation is schematically outlined in **Figure 24**.

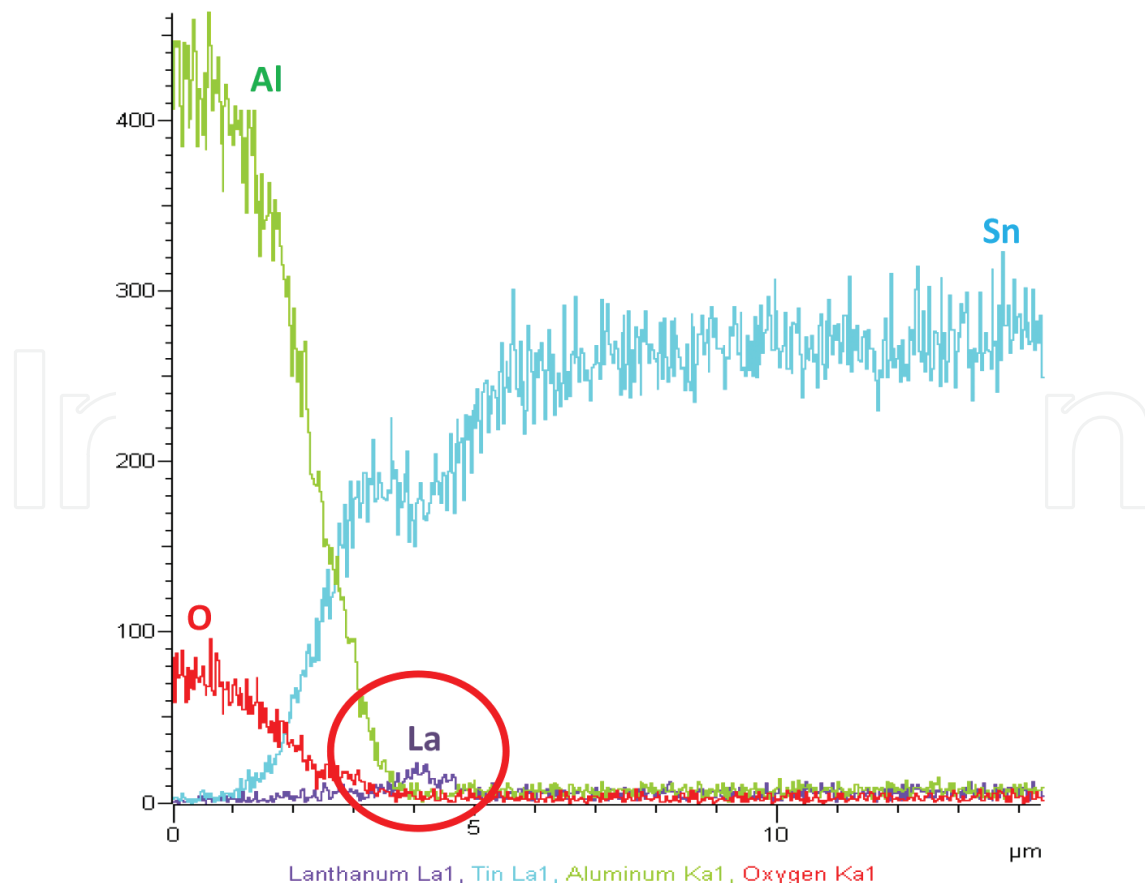


Figure 22. Concentration profiles of Al, Sn, La and O elements on the interface of Al_2O_3 ceramics/Sn2La solder.

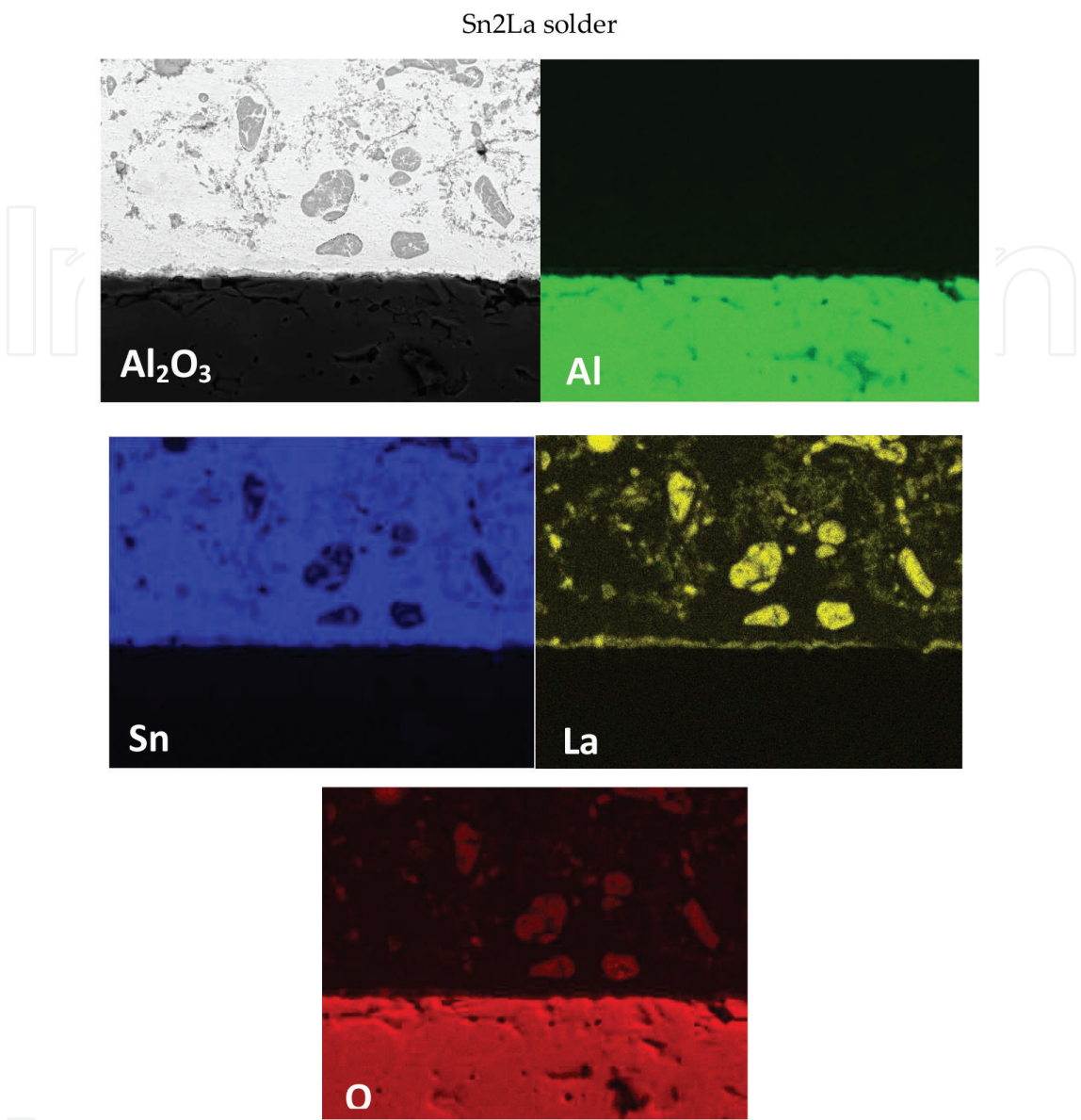


Figure 23. Planar EDX analysis of soldered interface of Sn2La/ Al_2O_3 .

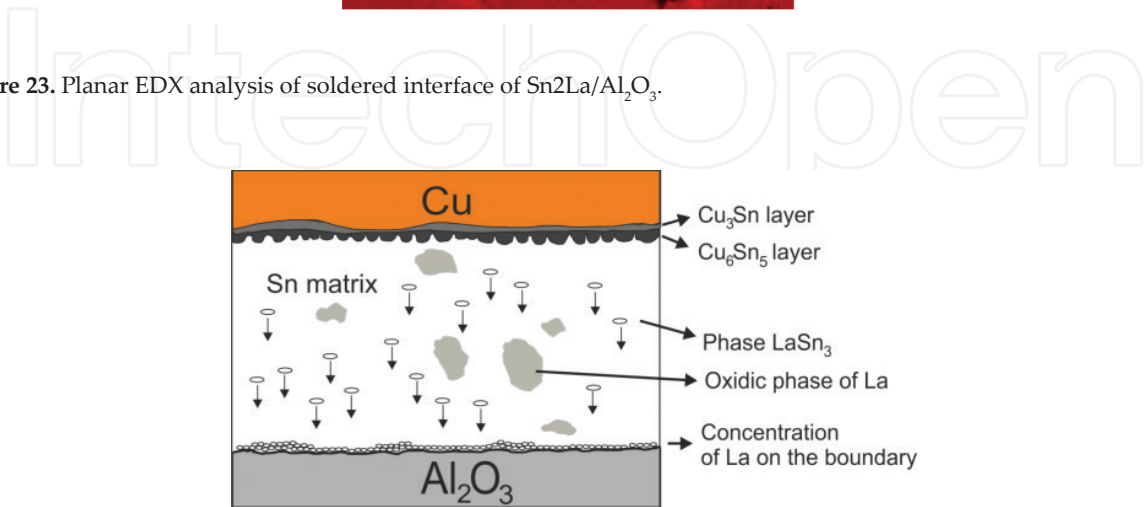


Figure 24. Mechanism of bond formation at UT activation of Sn2La2 solder.

The research was primarily oriented to soldering ceramic substrate of Al_2O_3 and a copper substrate. The experiments carried out in the study of shear strength of soldered joints were extended to other metallic materials (Al, Ni, Ti and CrNi steel) and SiC ceramics in order to show broader applicability of Sn2La solder.

Measurement was performed on four specimens of each material. The results of average shear strength of joints are documented in **Figure 25**. The lowest shear strength was observed on Al_2O_3 ceramics (7.5 MPa). Little higher strength of 13.5 MPa was observed on SiC ceramics. The highest strength, when regarding the metallic materials, was achieved with Al and Ni. The strength on copper substrate was 26.0 MPa.

The Sn2La solder has shown relatively great differences in shear strength on the metallic and ceramic materials. It can be generally said that the shear strength of joints in metallic materials is almost three times higher than in the case of ceramic materials.

From the results of analysis of transition zone of soldered joints, it may be concluded that the bond with metallic material is of metallurgical-diffusion character. The bond with a ceramic material, namely Al_2O_3 (at soldering with solder containing La), is of adhesion character.

2.13. Active solder with titanium content

The aim of research [28] was to study the solderability of Al_2O_3 ceramics, silicon and copper at the application of solder type Sn-Ag-Ti activated by ultrasound. The interactions between solder, ceramic and silicon substrates were analysed. The shear strength of fabricated soldered joints was measured.

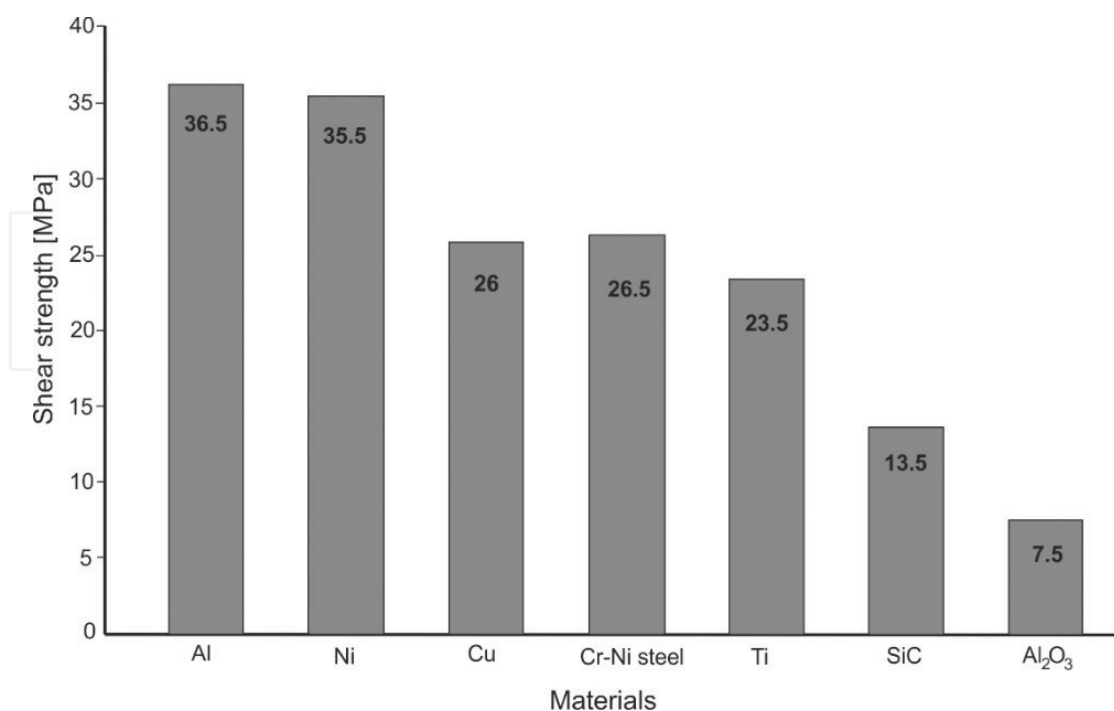


Figure 25. Results of measurements of shear strength in joints fabricated with Sn2La solder.

The Sn3.5Ag4Ti (Ce, Ga) solder was used for soldering. Soldered joints were fabricated with the application of mechanical activation by power ultrasound. Heating was realized by a hot-plate method. The soldering temperature was 280°C. The dwell time at soldering temperature was 30 s and the time of ultrasound acting was 5 s. The test specimens were prepared of Al_2O_3 ceramics, silicon as non-metallic material and Cu as metallic material.

The microstructure of solder type Sn-Ag-Ti is documented in **Figure 26**. It consists of tin matrix. The tin matrix contains unevenly distributed constituents of intermetallic Ti-Sn phases and fine needles of silver phase, Ag_3Sn , uniformly distributed along the tin grains. The presence of Ag_3Sn phase was proved by X-ray diffractometer (XRD) analysis.

XRD analysis revealed also the Ti-Sn phases. Actually identified were the Ti_6Sn_5 and Ti_2Sn_3 phases, where Ti_6Sn_5 phase was mostly represented. The formation of individual titanium phases depends on manufacturing the temperature of the solder, the amount of titanium added to solder and also the way of Ti addition to solder during its manufacture.

2.14. Analysis of soldered joint of Sn-Ag-Ti/ Al_2O_3

The microstructure of Sn-Ag-Ti solder/ Al_2O_3 ceramics is documented in **Figure 27**. A pronounced transition zone, reaction layer with an average thickness of 2.6 μm , is formed in the interface.

The energy-dispersive X-ray spectroscopy (EDX) analysis of chemical composition has revealed that the reaction layer (**Figure 28**) contains 5.35 wt.% Al; 37.33 wt.% Ti; 2.84 wt.% Ag and 54.48 wt.% Sn. The linear course of concentration of individual elements is documented in **Figure 26**.

During soldering process, the titanium from solder is distributed to the interface with ceramic material, where a reaction layer is formed, which ensures the wettability of Al_2O_3 ceramics. An oxidation-reduction reaction takes place between the active solder and ceramic material at the formation of reaction products, which allow the wetting of ceramics by an active solder (**Figure 28**).

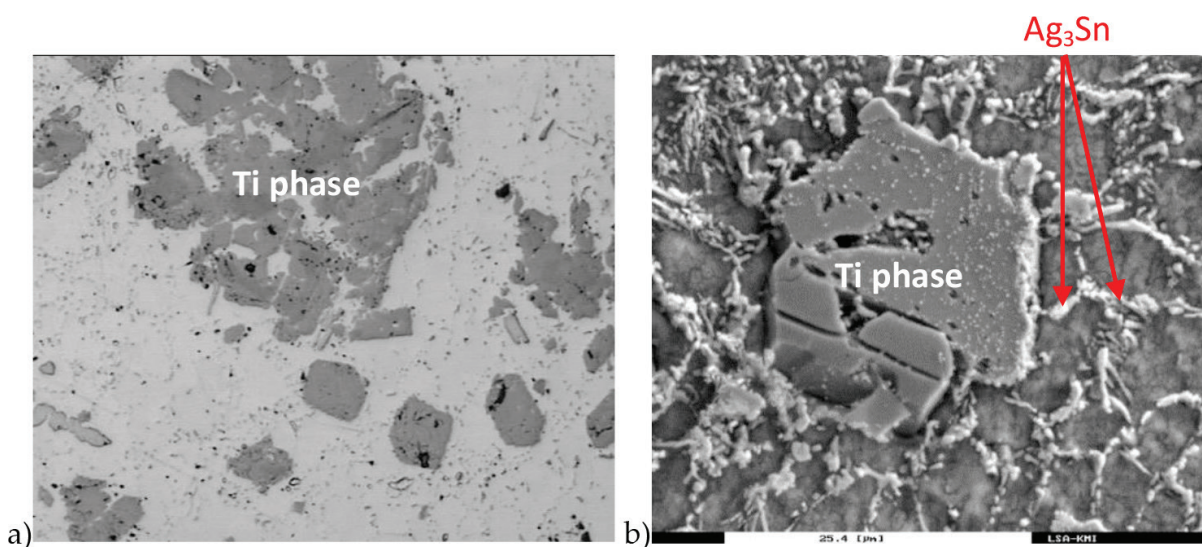


Figure 26. Microstructure of Sn-Ag-Ti solder (a) in polished condition, (b) after etching of tin matrix.

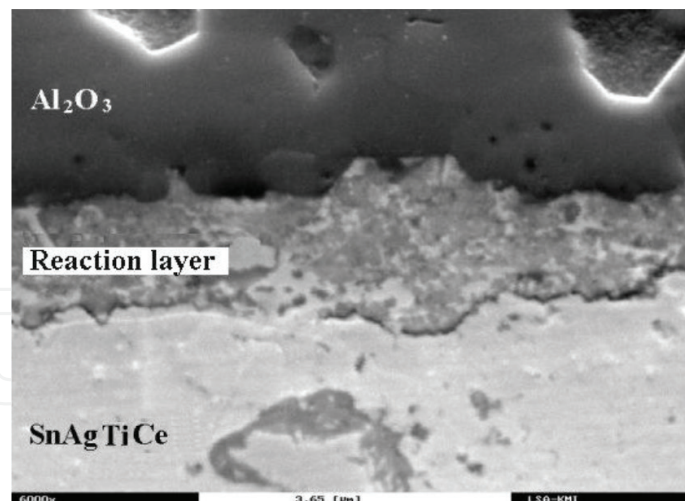


Figure 27. A detailed view of reaction layer in Al_2O_3 /Sn-Ag-Ti interface.

2.15. Analysis of Sn-Ag-Ti/Si-soldered joint

The interface of Si/Sn-Ag-Ti solder joint can be seen in **Figure 29**. The Ag_3Sn phase is segregated along the grain boundaries of tin matrix of the solder. This phase increases the strength of soldering alloy type Sn-Ag-Ti. Also, the formation of a pronounced reaction layer, 1–2 μm in thickness, may be seen in **Figure 29**. The formation of this layer in the consequence of interactions is between the active element (Ti) and the surface of silicon substrate. Titanium is segregated to interface with silicon during the soldering process. The products of interaction ensure the wetting of silicon and bond formation. The diffusion mechanism takes place there. The ultrasound exerts two effects in this case, namely it speeds up the Ti diffusion and disrupts the substrate surface by the cavitation erosion.

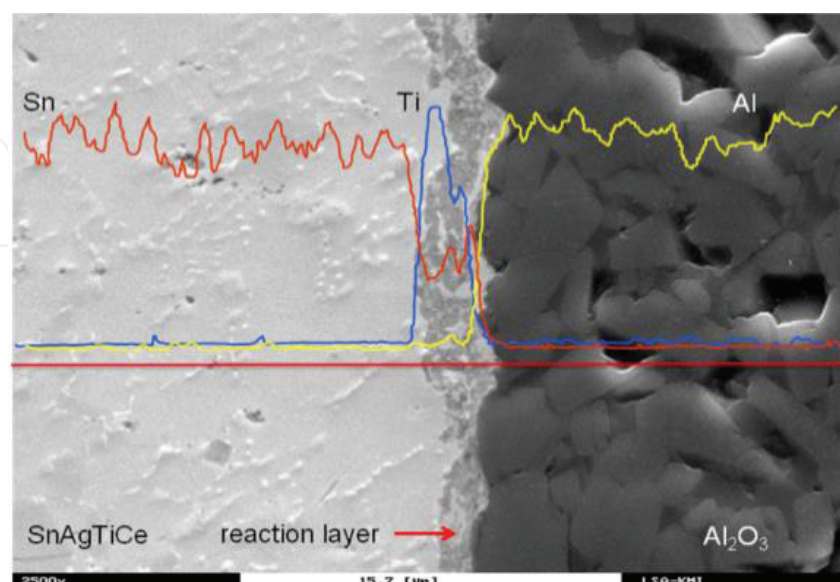


Figure 28. Interface of the soldered joint of Al_2O_3 /Sn-Ag-Ti solder.

The formation and composition of reaction layer may be well observed on the planar distribution of elements attained by EDX analysis. **Figure 30** shows the map of elements in the interface of soldered joint. In **Figure 30**, we may also see the segregation of Ti on Si/Sn-Ag-Ti interface; 28 wt. % Ti was observed in the reaction zone, while the balance consisted of silicon.

2.16. Analysis of Sn-Ag-Ti/Cu-soldered joint

In case of solder type Sn-Ag-Ti, the main role in bond formation with Cu substrate is played by tin. The Cu_3Sn , Cu_6Sn_5 phases were identified in the solder/Cu substrate interface in all cases, which are growing in the direction from the phase interface to solder matrix. The Cu_3Sn phase is closer to Cu substrate and the Cu_6Sn_5 phase is in contact with Sn-Ag-Ti solder.

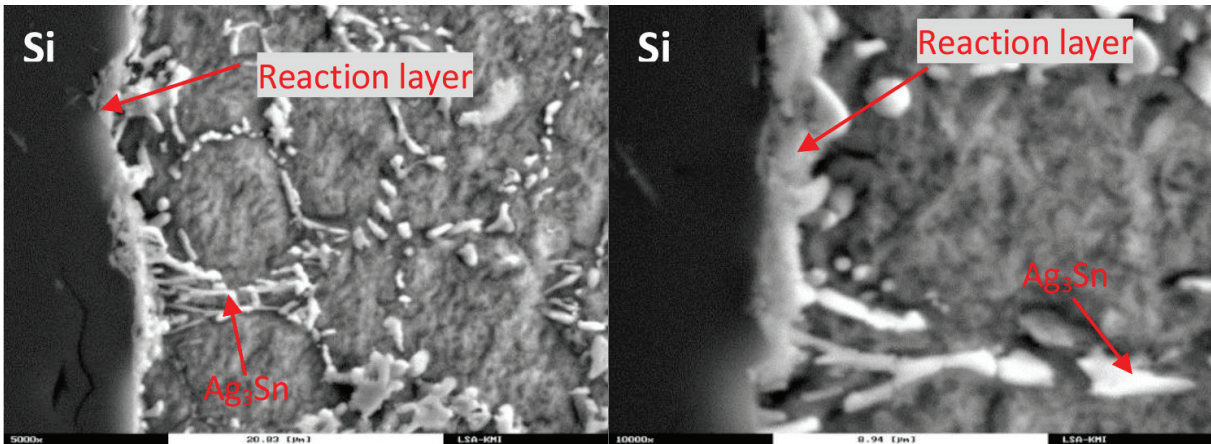


Figure 29. Reaction layer on Si/Sn-Ag-Ti solder interface.

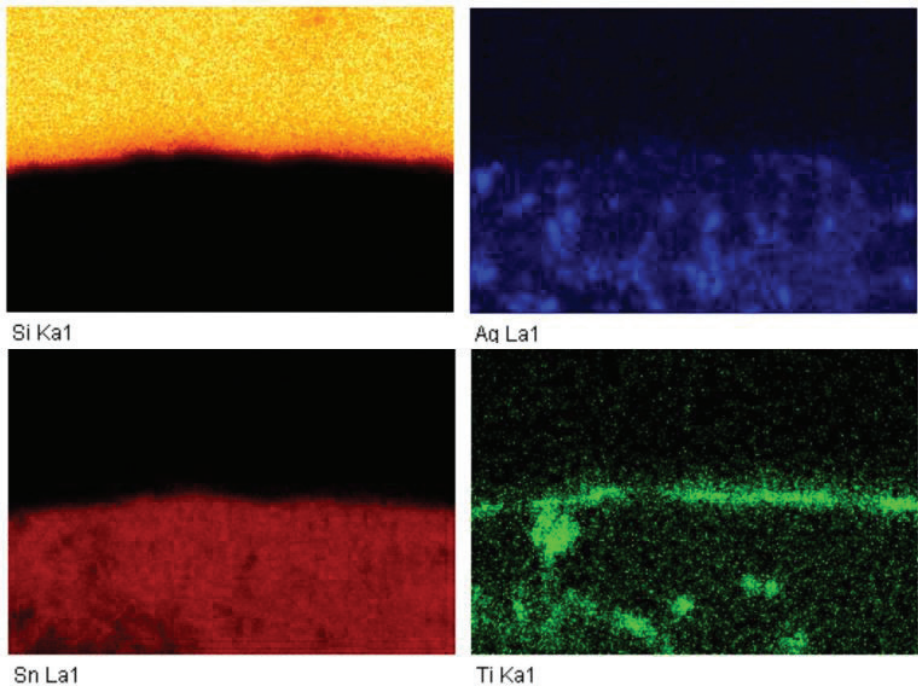


Figure 30. Map of Si, Ag, Sn and Ti elements in the interface of Si/Sn-Ag-Ti joint.

Massive transition phases of Cu_6Sn_5 were formed, up to 12 μm in width. The Cu_6Sn_5 phase has an elongated acicular shape as shown in **Figure 31**.

2.17. Shear strength of soldered joints

The research of this study was primary oriented to soldering of ceramic Al_2O_3 substrate, silicon substrate and copper substrate. However, the experiments performed in the study of shear strength of soldered joints were extended to other metallic materials (Al, Ni, Ti and CrNi steel type AISI 316) and SiC ceramics in order to approve wider applicability of Sn-Ag-Ti solder.

The measurement was performed on four specimens of each material. The results of average shear strength are documented in **Figure 32**. The lowest shear strength was observed with silicon, 23.0 MPa. Higher strength, attaining 33.0 MPa, was observed with Al_2O_3 , whereas with copper the shear strength attained even 35.1 MPa.

The Sn-Ag-Ti solder exerted small differences in shear strength on metallic and ceramic materials. It may be generally said that the shear strength of joints in metallic materials is comparable with the shear strength attained on ceramic materials.

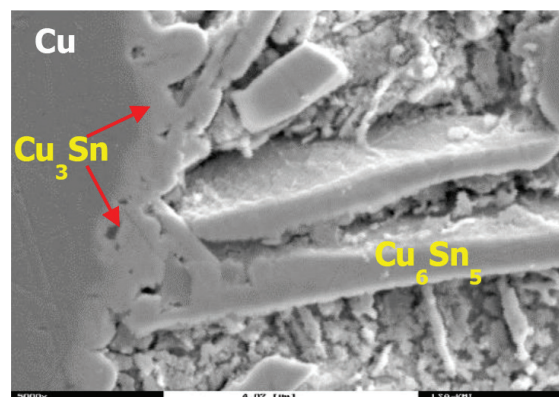


Figure 31. Analysed microstructure in interface of Cu/Sn-Ag-Ti solder joint.

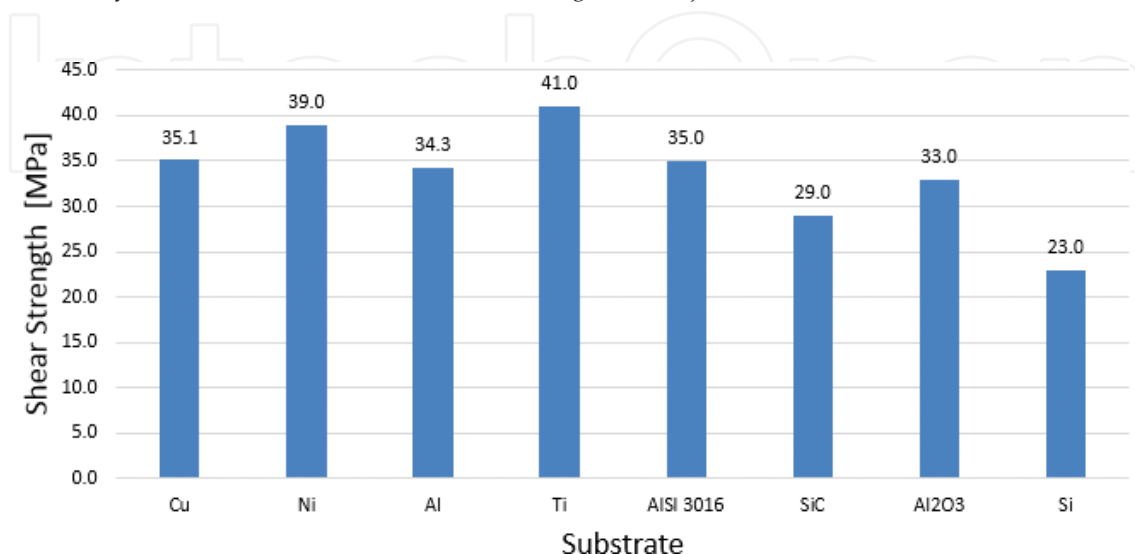


Figure 32. The shear strength of joints fabricated with Sn-Ag-Ti solder.

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