Study of Active Soldering of Al_2O_3 Sputtering Targets on Copper Substrates

Martin Provazník, Roman Koleňák, Miloš Baľák, Miroslav Marcian

***Abstract* – The work deals with the technology of joining ceramic Al_2O_3 targets with copper. The active solder types Sn3.5Ag4Ti(Ce, Ga), Sn2Ti, and Bi25In18Sn were analysed in this study. These solders were selected owing to their acceptable melting point and possibility of mechanical activation. The highest melting point, namely 235.8 °C, was achieved by Sn2Ti solder. The phases Ti_6Sn_5 and Ti_3Sn were observed in this solder. In Sn3.5Ag4Ti(Ce, Ga) solder, besides the phases of the Sn–Ti system, the silver phases Ag_3Sn and Ag_3Ti were also observed. In Bi25In18Sn solder the phases $BiIn_2$, In_3Sn, $InSn_4$, and BiIn were found. The shear strength of fabricated joints varied from 7 to 35 MPa. The highest strength of joints was achieved with Sn3.5Ag4Ti(Ce, Ga) solder. The lowest shear strength was attained with Bi25In18Sn solder. In the case of active solders, Ti formed a continuous layer of reaction products consisting of Ti–O systems on the joint boundary of Al_2O_3 ceramics. In the case of Bi25In18Sn solder, In also contributes to joint formation. The layers of reaction products alter the surface energy of ceramic substrate and allow its wetting with solder.**

Index Terms* – *Al_2O_3 sputtering target, active solder

I. INTRODUCTION

THE presented work deals with soldering ceramic targets with active solders. Older methods applied for the fabrication of ceramic-metallic targets included metallization of Al_2O_3 substrate by molybdenum and manganese followed by nickel coating and sintering at high temperatures [1]. To prevent degradation of ceramic material due to the effect of high temperatures, technologies making use of active metals are used for soldering the targets. One of the possibilities seems to be physical vapor deposition (PVD) sputtering of ceramic materials by layers of active metals (Ti, Zr, Hf) followed by coating with a thin layer of precious metals (Au, Pd, Pt). The formed layer allows a good wetting by solders and brazing alloys as well [2]. In present practice, direct soldering with active solders is preferred [3], [4].

Active solders contain an active element, most often Ti or Zr [5]. The active element reacts with the surface of the ceramic material owing to mechanical activation, resulting in the formation of a continuous reaction layer. This layer allows wetting of ceramic material and thus joint formation [6] – [8]. The active solders can be protected against excessive oxidation of their active element by addition of elements with higher affinity to oxygen (Ce, La). At the same time additions also enhance wetting; for example Ga is added to solder alloys [9], [10].

In this study the following solders with active element content were used: Sn3.5Ag4Ti(Ce, Ga), Sn2Ti, and a bismuth solder type Bi25In18Sn, with melting points of up to 250 °C. The aim of the work is to characterise the mechanism of soldered joint formation and to determine the most suitable alloy for joining targets of Al_2O_3 ceramics. The possibility of direct soldering by application of ultrasonic activation is an important criterion in solder selection, which is a condition ensuring a good wetting of ceramic materials.

II. EXPERIMENTAL

For identification of the composition and distribution of the active element in active solder and, its distribution and interaction with the boundary of parent metals, the solders were subjected to the following analyses.

The microstructure of analysed solders was studied by electron scanning microscopy (SEM) by use of a Tescan Vega TS 5130 MM microscope. The qualitative and semi-quantitative chemical micro-analysis of solder was performed by an INCA Energy 300 X-ray micro-analyser. For identification of the phase composition of solder, X-ray diffraction analysis was carried out. This was realised on the samples of dimensions 10 × 10 mm on Philips PW 1710 equipment with X'Pert HighScore evaluation software.

In order to prevent excessive oxidation of solders heated in the air without flux, the exact melting points were determined by use of differential calorimetry (DSC). These measurements were performed on PerkinElmer DSC7 equipment in a shielding atmosphere of N_2. The results of measurements were assessed by NETZSCH Proteus Pyris 3.0 software.

The shear strength was determined at room temperature on LabTest 5.250SP1-VM equipment in accordance with the EN 10002 standard. The results of this test define the attained strength of the bond in its phase boundary and also the solder's elasticity.

A. *Preparation of samples*

The soldered joints were fabricated by use of mechanical activation with power ultrasound. Heating was realised via a

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hot plate with thermostatic regulation. The soldering temperature was 20 °C above the liquidus temperature of the tested solder. The dwell time at the soldering temperature was 30 s and the time during which ultrasound acted upon the soldered joint was 5 s. The test samples were made of Al_2O_3 ceramics with 3N purity and copper with 99.94% purity in the form of rings Ø 15 mm in diameter and 1.5 mm in thickness. The scheme for soldering by the hot plate method with ultrasound assistance is shown in Fig. 1.

The ultrasound activation of solders is necessary to wetting of ceramic materials. On the metal side ultrasound replaced a flux soldering [11].

Soldering was performed by the use of UT equipment with 40 kHz frequency, 400 W output power, and 2 µm amplitude. The specimen for shear strength testing is shown in Fig. 2-a. The procedure for preparation of specimens for shear strength testing was as follows (Fig. 2-b). A forming ring is laid freely on the parent metal, which serves as a mould for the liquid solder. The forming ring must be centred coaxially with the centre of the substrate metal. Their mutual position is secured by sliding a clamp, which, simultaneously with a slight pre-stressing, assures a proper setting of the forming ring on the substrate.

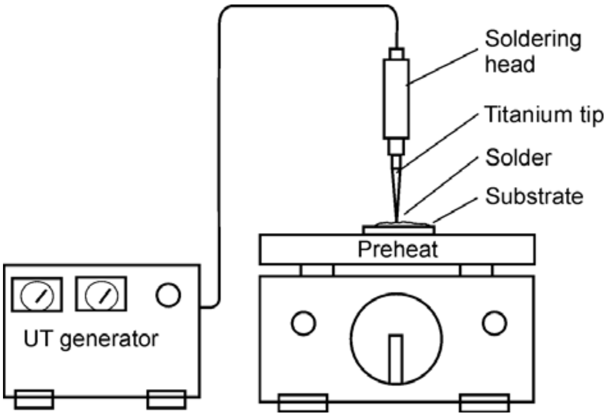

Fig. 1. Scheme of equipment for ultrasonic soldering.

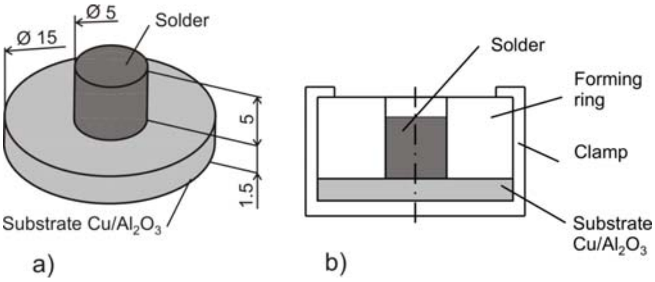

Fig. 2. Test specimen
a) shape and dimensions, b) preparation procedure.

B. *Shear test*

To alter the acting direction of axial tension force on the test specimen a newly developed shearing jig was applied. The shear mechanism with shear force acting on the test specimen during the test is shown in Fig. 3. The shearing jig ensures a uniform loading of the specimen by shear in the boundary plane of the solder and parent metal. The steady testing rate was 2 mm/min. The criteria for test termination were s = 7 mm; dF = 99%.

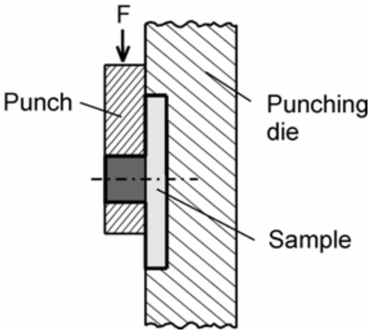

Fig. 3. Principal scheme of shear test.

III. RESULTS

A. *Results of DSC analyz*

DSC analysis allowed the melting interval of the studied solders to be determined exactly. The lowest melting point, in the range from 60.3 to 63.6 °C, was attained with Bi25In18Sn solder (Fig. 4). Figure 5 shows the results of DSC analysis of Sn3.5Ag4Ti(Ce, Ga) solder, whose melting interval was 221.4 to 224.6 °C. The Sn2Ti solder shown in Fig. 6 exerted the highest melting temperature: in the range from 232.1 to 236.5 °C. Each of the studied solders passed through three heating cycles. The results from the third run were included in the results of DSC analyses shown in Table 1.Calibration and verification of attained values was performed by the use of Bi, In, and Sn etalon metals with 4N purity. Analyses were realised in a shielding atmosphere of nitrogen with 99.9999% purity at 20.0 ml/min flow rate.

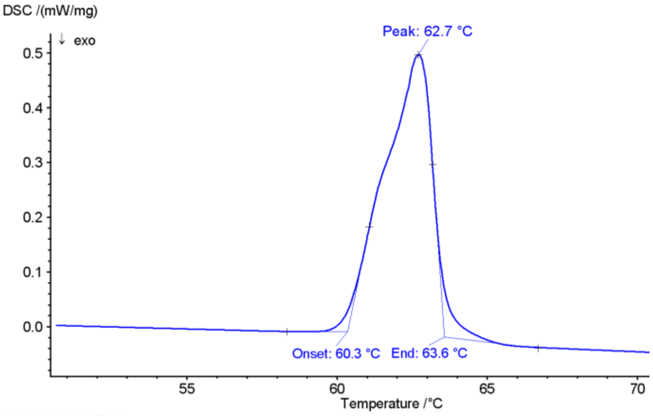

Fig. 4. DSC curve of Bi25In18Sn solder on heating 5 °C /min.

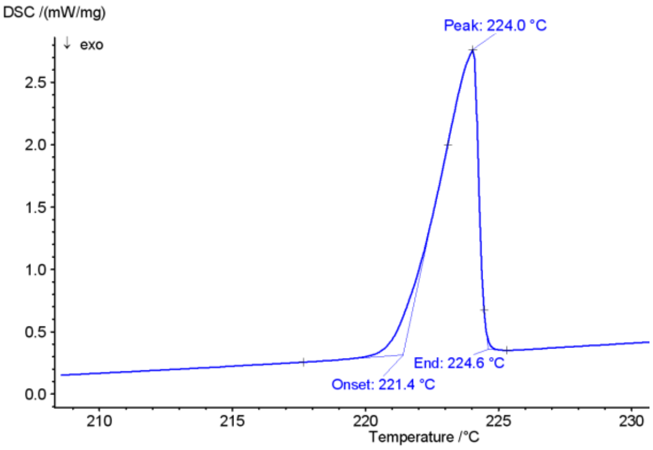

Fig. 5. DSC curve of Sn3.5Ag4Ti(Ce, Ga) solder on heating 5 °C /min.

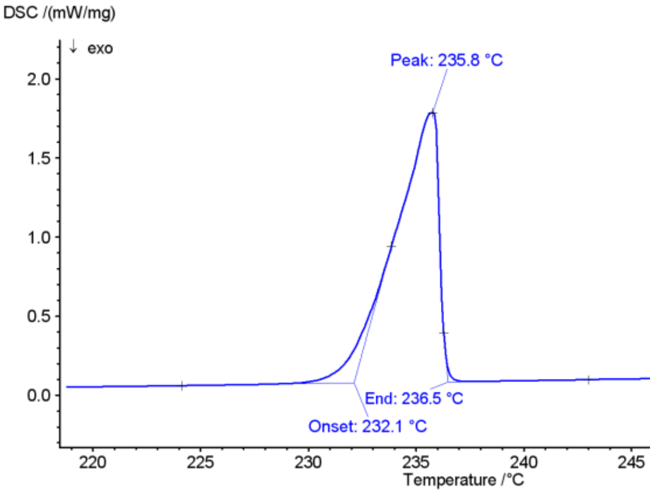

Fig. 6. DSC curve of Sn2Ti solder on heating 5 °C /min.

TABLE I
The results of DSC analyz

Solder	Bi25In18Sn	Sn3.5Ag4Ti(Ce, Ga)	Sn2Ti
Heating rate	5 °C /min	5 °C /min	5 °C /min
Weight	22 mg	24mg	31 mg
Onset temperature [°C]	60.3	221.4	232.1
Peak temperature [°C]	62.7	224.0	235.8
End temperature [°C]	63.6	224.6	236.5
Published Solidus temperature [°C]	59.8 [12]	217.8 [6]	230.5 [8]
Published Liquidus temperature [°C]	61.3 [12]	228.9 [6]	235.5 [8]

B. *Results of phase and microscopic analyz*

The phase composition of solders prior to heating above liquidus temperature was ascertained by X-ray diffraction analysis. This completes the qualitative chemical microanalysis and identifies the phases where an active element is present.

Diffraction analysis performed on Bi25In18Sn solder specimen (Fig. 7) revealed the presence of the following phases: (Bi), (Sn), (In), $BiIn_2$, In_3Sn, $InSn_4$, and BiIn. This solder shows a fine and uniformly distributed multiphase structure. The grey matrix contains on average 80% Bi – 12.5% In – 7.5% Sn. The white phase is formed of Bi – In (32.5% In – 67.5% Bi) phases. The dark-grey constituents show an increased tin content (13.5% Bi – 6.5% In – 80% Sn).

Figure 8 shows a record from the diffraction analysis of Sn3.5Ag4Ti(Ce, Ga) solder. The following phases were observed: Ti_6Sn_5, Ag_3Sn, Ag_3Ti, and Ti_3Sn. The solder consists of a tin matrix, where constituents of intermetallic Ti-Sn phase are non-uniformly distributed and Ag_3Sn and Ag_3Ti (93% Sn – 6.5% Ag – 0.5% Ti) phases are also present. The dark-grey phases contain on average 31.5% Ti – 68.5% Sn, whereas the dark zones are formed of pure Ti. Phase analysis did not prove the presence of cerium and gallium compounds. These elements occur in the solder just below the detectability limit.

By diffraction analysis performed on Sn2Ti solder specimen (Fig. 9), the presence of Ti_6Sn_5 and Ti_3Sn phases was observed. The solder microstructure consists of a tin matrix (100% Sn) where non-metallic phases of the Ti–Sn system are non-uniformly distributed. The coarse dark-grey phases contain 13.8% Ti – 86.2% Sn, and the smaller light-grey phases contain 3.6% Ti – 96.4% Sn.

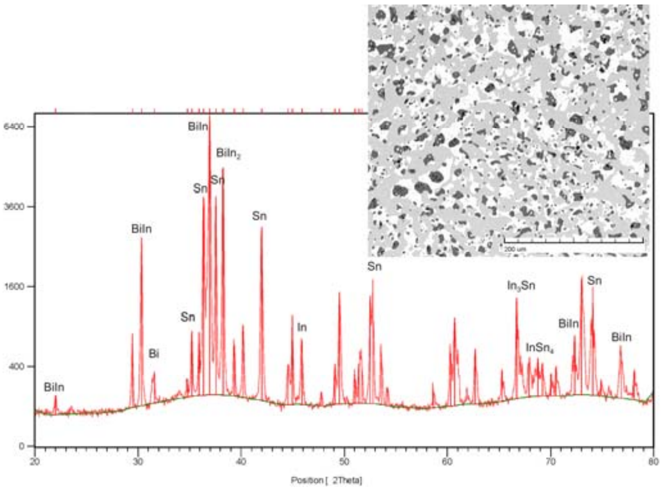

Fig. 7. XRD patterns of Bi25In18Sn solder.

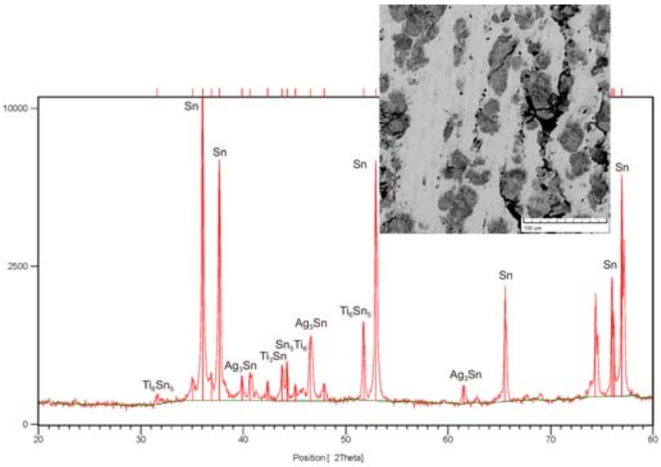

Fig. 8. XRD patterns of Sn3.5Ag4Ti(Ce, Ga) solder.

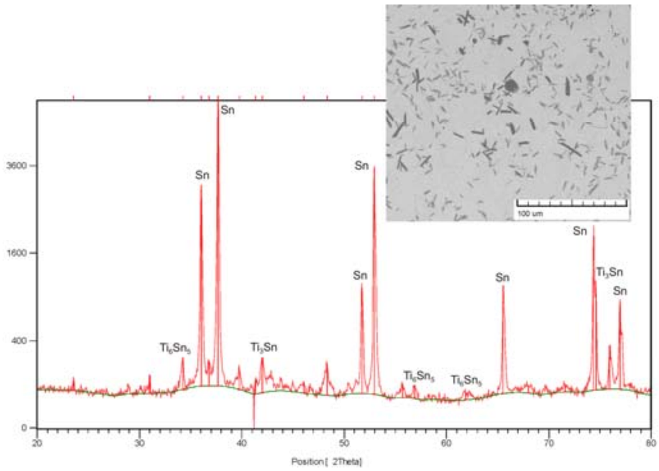

Fig. 9. XRD patterns of Sn2Ti solder.

C. *Results of shear test*

Figure 10 shows the documented values of shear strength of the analysed soldered joints. The aim of measurement was to identify the solder with the best strength properties from among the choice of alloys.

The highest strength on the copper and ceramic substrate was achieved with Sn3.5Ag4Ti(Ce, Ga) solder, and at the same time, this solder showed the smallest difference between the values of shear strength on the side of the ceramic and metal among all solders investigated. The lowest values of shear strength were attained with Bi25In18Sn solder on both the copper and the Al_2O_3 ceramics side. The Sn2Ti solder showed average values of shear strength.

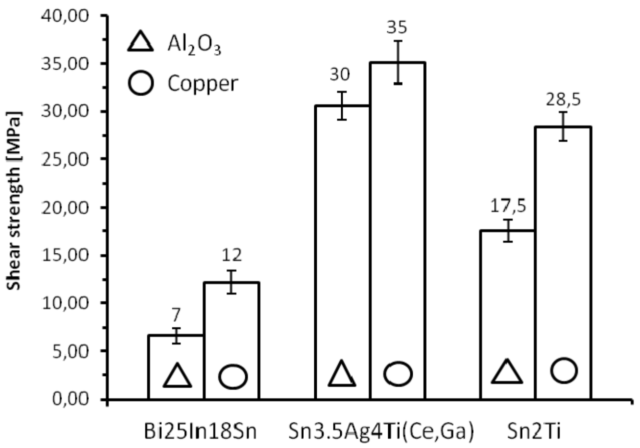

Fig. 10. Shear strength of ceramics/ceramics and ceramics/metal joints.

D. *Analyz of solder- Al_2O_3 joints*

A longitudinal crack was observed on the Bi25In18Sn–Al_2O_3 joint boundary (Fig. 11) occurring over the entire length of the specimen. This crack was formed during metallographical preparation of the specimen owing to the low plastic and elastic properties of the solder used. Based on the REM/EDX analysis performed it can be supposed that In participates predominantly in joint formation by formation of indium oxide In_2O_3.

A continuous reaction layer containing Ti was observed on the Sn3.5Ag4Ti(Ce, Ga) – Al_2O_3 joint boundary (Fig. 12). This reaction layer allows wetting of the ceramic material and the tin matrix of the solder and at the same time guarantees sufficient plastic properties of the soldered joint. A slightly increased concentration of cerium was also observed on the boundary. It was impossible to register the presence of gallium and its effect upon joint formation.

Figure 13 shows the boundary of the Sn2Ti – Al_2O_3 joint. The map of the planar distribution of elements obviously suggests that the Ti active element contributes significantly to joint formation. It forms a continuous reaction layer on the joint boundary similarly to in the case of the Sn3.5Ag4Ti(Ce, Ga) solder. This reaction layer is formed due to the reaction of Ti with oxygen from ceramics in the formation of titanium oxides, which alter the surface energy of ceramics and thus allow its wetting by solder.

All solders attained very good wettability on Al_2O_3 substrate after activation with ultrasound. Therefore the resultant joint strength is also affected by the mechanical anchoring, depending on the roughness and porosity of the ceramic surface.

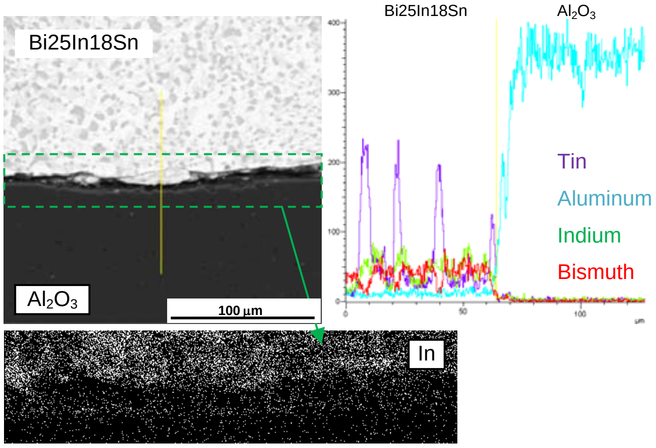

Fig. 11. Line scanning on the boundary of Bi25In18Sn – Al_2O_3.

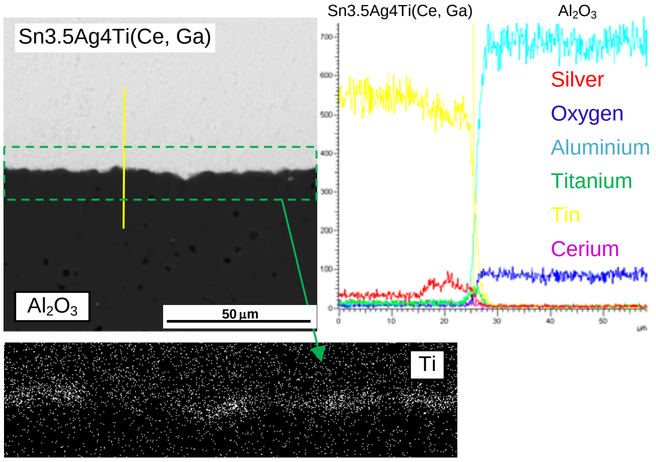

Fig. 12. Line scanning on the boundary of Sn3.5Ag4Ti(Ce, Ga) – Al_2O_3.

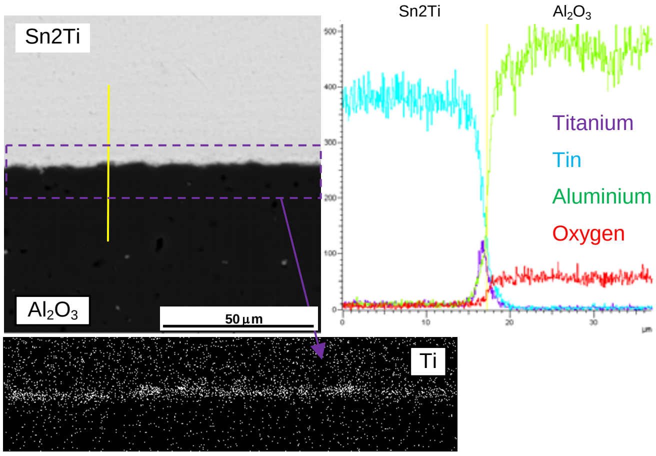

Fig. 13. Line scanning on the boundary of Sn2Ti – Al_2O_3.

E. Analyz of solder - Cu joints

A continuous reaction zone is formed on the Bi25In18Sn solder and copper boundary (Fig. 14). Based on the analyses performed, we suppose that copper interacts with the tin and indium compounds in the solder matrix. A thinner, non-wettable phase rich in Cu (Cu_3Sn) followed by Cu_6Sn_5 phase is also formed on the joint boundary.

Figure 15 shows the Sn3.5Ag4Ti(Ce, Ga) – copper substrate boundary. Sn exerts a decisive effect on joint formation. Cu is dissolved in the Sn matrix and forms Cu_3Sn and Cu_6Sn_5 phases that grow in the direction from the phase boundary to the solder matrix.

On the boundary of the Sn2Ti solder and copper (Fig. 16) a continuous layer of reaction products is formed owing to the dissolution of Cu in the Sn matrix. We suppose that the formation of similar Cu_6Sn_5 and Cu_3Sn phases occurs as in the case of Sn3.5Ag4Ti(Ce, Ga) solder. The records of EDX analyses suggest that Ti does not contribute to joint formation but is locally bound in the dark phases in the solder matrix.

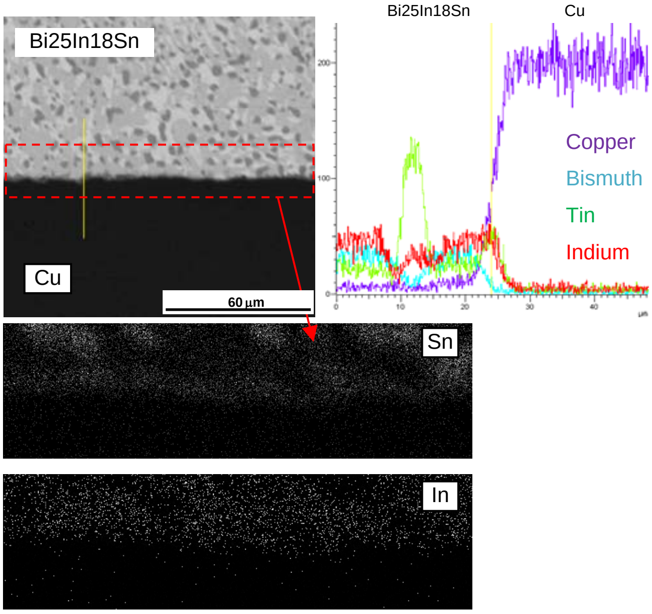

Fig. 14. Line scanning on the boundary of Bi25In18Sn – Cu.

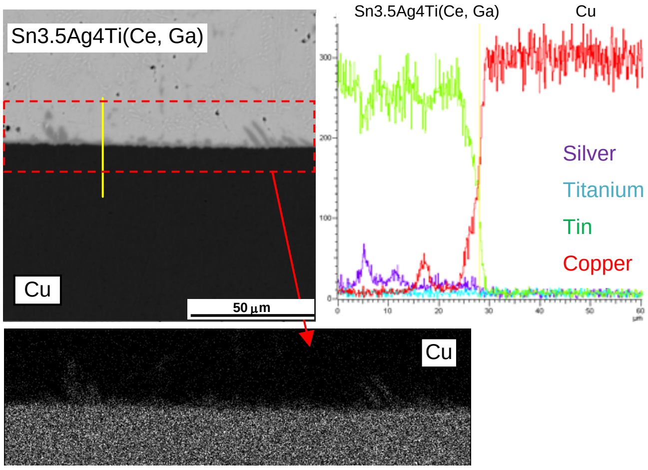

Fig. 15. Line scanning on the boundary of Sn3.5Ag4Ti(Ce, Ga) – Cu.

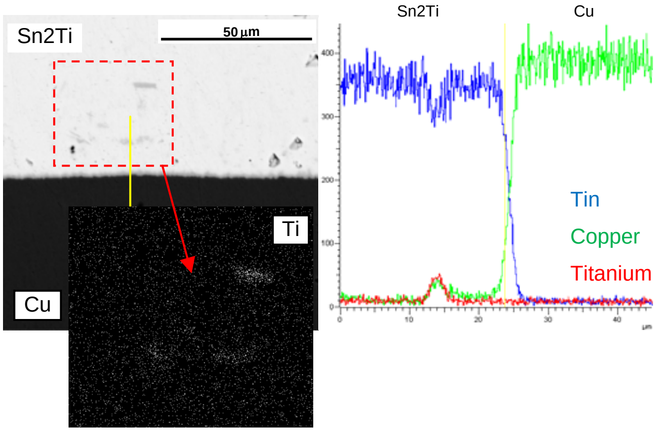

Fig. 16. Line scanning on the boundary of Sn2Ti – Cu.

IV. CONCLUSION

The aim of the work was to design a solder suitable for soldering bimetallic targets by direct soldering of Al_2O_3 ceramics with copper. Selection criteria for the set of analysed solders included a suitable melting point, possibility of direct soldering with UT activation, sufficient solder strength, and capability to compensate the inner stresses caused by differences in the thermal expansion of joined materials.

The Sn2Ti solder attained the highest melting point, 235.8 °C, and contained mostly Ti_6Sn_5 and Ti_3Sn phases. The same phases together with silver Ag_3Sn and Ag_3Ti phases were observed in Sn3.5Ag4Ti(Ce, Ga) solder. The highest joint strength was achieved with Sn3.5Ag4Ti(Ce, Ga) solder. The strength reached 30 MPa on Al_2O_3 and 35 MPa on copper.

A continuous diffusion zone of reaction products of tin and indium was observed in analyses of Bi25In18Sn – copper joints. A diffusion zone of reaction products of the Sn – Cu system was observed in analyses of joints fabricated by use of Sn3.5Ag4Ti(Ce, Ga) and Sn2Ti solders. Formation of Cu_6Sn_5 and Cu_3Sn is supposed. No diffusion zone was observed on the solder – Al_2O_3 boundary. Indium contributed to the formation of a ceramics – Bi25In18Sn solder joint.

Titanium exerted a significant effect on the formation of joints fabricated with active solders, while its increased concentration was observed mainly at the phase boundary. By reaction of Ti with the ceramics surface, titanium compounds are formed which alter the surface energy of the ceramics, and their wetting with solder is thus allowed.

The chemical bonding of the ceramic material surface is simultaneously accompanied by mechanical bonding through the mechanism of solder spreading into the intergranular space of the ceramic substrate. Based on the analyses performed, it may be stated that among the entire choice of solders compared, the conditions of solderability of ceramic Al_2O_3 targets were best met by the Sn3.5Ag4Ti(Ce, Ga) solder.

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