Study of Direct Bonding of Ceramic and Metallic Materials with Zn4Al Solder

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Abstract: The aim of this work was to evaluate the direct bonding of Al2O3, SiC ceramics and Cu substrates. Joints were fabricated by using 40 kHz frequency ultrasound. The Zn4Al solder wetted all materials studied and joints of good quality were produced. The shear strength attained with Al2O3 ceramics was 81 MPa. The strength with SiC ceramics was slightly lower at 65 MPa. In a copper substrate, we observed shear strengths of 84 MPa.

Keywords: soldering; ceramic; metallic; microstructure; strength

1 Introduction

Zn-based solders belong to the group of solders applicable for higher application temperatures. Currently, soldering technology at these temperatures is widely used and imparts irreplaceable properties to the resulting product for high thermal conductivity and reliability. These solders are mainly used in electronics, as well as, in the automotive, space, aviation and power industries.

In the study [1], we investigated the direct bonding of SiC ceramics with ultrasound assistance. The ceramic SiC substrates were soldered in the air with Zn8.5Al1Mg solder at a temperature of 420°C. The shear strength of joints increased with longer periods of ultrasound exposure. The highest strength (148.1 MPa) was achieved at ultrasound periods lasting for 8s. A new amorphous layer 2 to 6 nm thick was formed on the boundary between the solder and substrate. The atoms from eroded SiO_2 layers from SiC substrates quickly diffused to the solder, owing to the jet effect caused by ultrasound. The strong bond between SiC substrate and Zn-Al-Mg solder is attributed to the transfer of SiO_2 mass to Zn-Al-Mg solder by induced cavitation erosion.

Direct bonding of sapphire (a crystalline form of Al_2O_3) by ultrasound, with the application of Sn10Zn2Al solder was the subject of a study [2]. It was found that ultrasound supported the oxidation reaction between Al from the solder and sapphire substrate. A nano-crystalline α-Al_2O_3 layer (2 nm thick) was formed in the Sn-Zn-Al/sapphire boundary during soldering in the air at a temperature of 230°C. The shear strength of joints measured 43 to 48 MPa, which is a relatively high value when compared to other Al_2O_3 ceramic joints fabricated with active Sn solders and the addition of Ti and/or lanthanides [3, 4, 5].

The aim of our work was to study the direct bonding of Al_2O_3, SiC ceramics and copper substrate. Contrary to previous studies, the close-to-eutectic solder based on Zn-Al, (actually Zn4Al) was used. This solder is used for fluxless soldering of aluminum and its alloys. Ultrasonic soldering with direct ultrasound action was employed through the layer of molten solder.

2 Experimental

Zn solder with 4 wt% of Al was used in the experiments. The solder was manufactured in cast state in a high vacuum of 10^{-4} Pa. The procedure was as follows: the calculated charges of alloy components were inserted into a graphite boat. The boat with the charge was placed into a horizontal tube resistance vacuum furnace so that the boat was situated in the heating zone. The tube could be flushed with Ar, owing to a flange on its edge and an outlet on its end.

For Zn-based solders it is more suitable to prepare them in overpressure of Ar, due to evaporation. The charge was exposed to temperature above 450°C. Homogenization of individual components took place at this temperature.

Experiments used the substrates of the following materials:

- Metallic substrate of Cu with 4 N purity in the form of rings, in dimensions Ø 15 x 1.5 mm
- Ceramic Al_2O_3 substrate, with 2N5 purity in the form of Ø 15 x 2 mm rings (manufacturer Glynwed, GmbH, designation Degussit Al23),
- Ceramic SiC substrate in the form of Ø 15 x 3 mm rings (manufacturer CeramTec, GmbH, des. Rocar® SiC).

The combinations of materials shown in Fig. 1 were used for more detailed analysis.

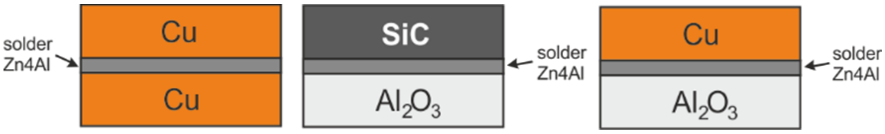


Figure 1
Analyzed combinations of Cu/Cu, SiC/Al_2O_3 and Cu/Al_2O_3 materials

Soldering was performed by Hanuz UT2 ultrasonic equipment with the parameters given in Table 1. The solder was activated by use of an encapsulated ultrasonic transducer consisting of a piezo-electric oscillating system and a titanium sonotrode with an Ø 3 mm end diameter. The scheme of ultrasonic soldering through the layer of molten solder is shown in Fig. 2. The soldering temperature was 20°C above the liquid temperature of the solder. Soldering temperature was checked by a continuous temperature measurement on the hot plate, using a NiCr/NiSi thermocouple.

Table 1

Soldering parameters

Ultrasound power	[W]	400
Working frequency	[kHz]	40
Amplitude	[μm]	2
Soldering temperature	[°C]	415 °C
Time of ultrasound activation	[s]	5

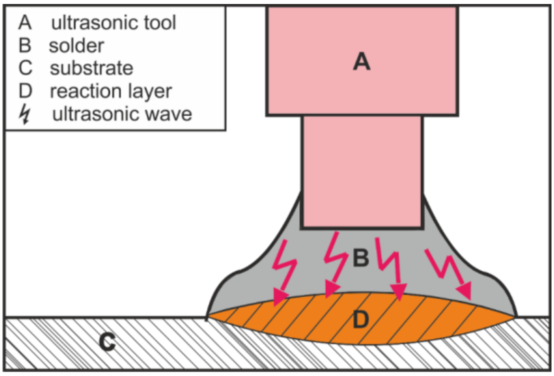


Figure 2

Ultrasonic soldering through the layer of molten solder

Soldering procedures took place in with the substrate heated at the soldering temperature deposited with a solder layer. Active ultrasound then acts upon the molten solder in the air without use of protective atmosphere for 5 s. After ultrasonic activation, the excessive layer of molten solder and the formed oxides are removed from the substrate surface. Both soldered substrates were prepared in the same way. The substrates with a deposited layer of molten solder were applied to each other so as to maintain contact during the molten phase. This assembly is then centered and the desired joint is achieved by slight compression. A graphic illustration of this procedure is shown in Fig. 3.

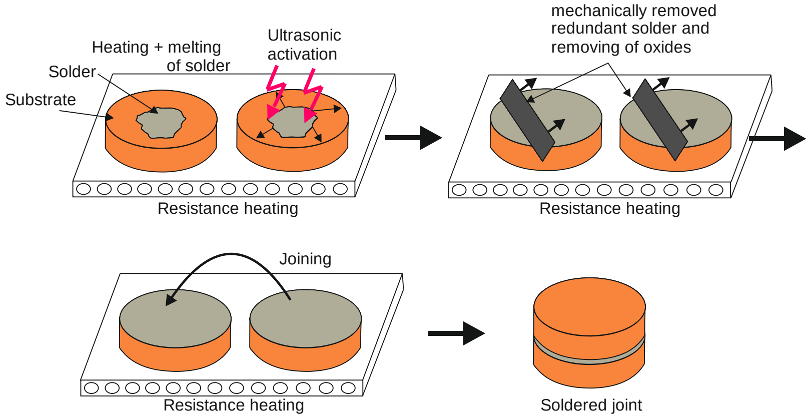


Figure 3
Procedure of joint fabrication by ultrasonic soldering

Metallographic preparation of specimens from the soldered joints was achieved by standard metallographic procedures used for preparation of specimens. The SiC emery papers with a granularity of 240, 320 and 1200 grains/cm^2 were used for grinding. The polishing was done by use of diamond suspensions with grain sizes: 9 μm, 6 μm and 3 μm. The final polishing was done using a type OP-S (Struers)polishing emulsion with a granularity of 0.2 μm.

Solder microstructure was observed by the aid of following:

- Neophot 32 light optical microscope, supplemented by a NIS-Elements, type E image analyzer
- Qualitative and semi-qualitative chemical analysis of the solder was performed by JEOL 7600 F equipment with a Microspec WDX-3PC X-ray micro-analyzer

X-ray diffraction analysis was used to identify the phase composition of the solder. It was applied on 10 x 10 mm solder specimens using a PANalyticalX´Pert PRO XRD diffractometer.

The DSC analysis of Zn4Al solder was performed on Netzsch STA 409 C/CD equipment in the Ar shielding gas with 6N purity.

A shear test was carried out to determine the shear strength of joints. Measurements were done on two ceramic (Al_2O_3 a SiC) and five metallic materials (Al, Ni, Ti, Cr-Ni steel, Cu) soldered using Zn4Al solder. The shear strength was determined on the versatile LabTest 5.250SP1-VM equipment. A shearing jig was used to change the direction of axial loading forces acting on the test specimen. This shearing jig ensured a uniform loading of specimens by shear in the plane of solder and substrate boundary (Fig. 4). The dwell time on soldering temperature during specimen fabrication was 30 s and the time of ultrasound acting was 5 s.

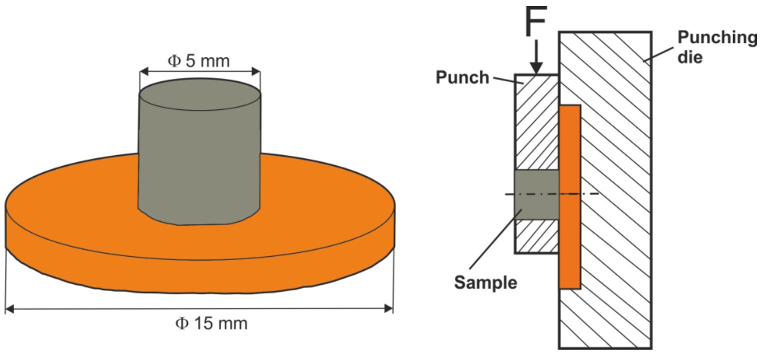


Figure 4
Test specimen for shear test and the scheme of specimen in the jig during the shear strength test [6]

3 Experimental Results

Analysis of ZnAl4 solder

Two solid solutions (Zn) and (Al) with a limited solubility occur in the binary Al-Zn system (Fig. 5). Owing to limited solubility, the eutecticum and eutectoid mixture of these solid solutions occurred in the system.

The matrix of Zn4Al solder (Fig. 6) was composed of great grains of the solid solution (Zn) with concentration of 98.68wt% Zn. A fine eutecticum, formed of solid solutions (Zn) + (Al) was segregated along the grain boundaries. The quantitative analysis of solder is given below in Fig. 6.

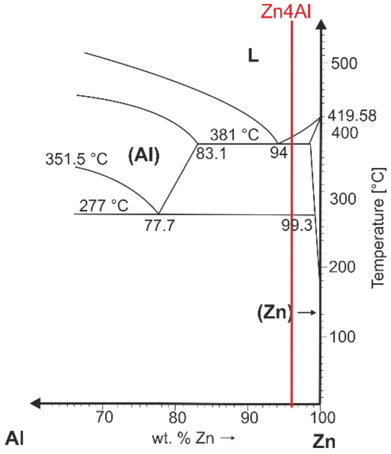
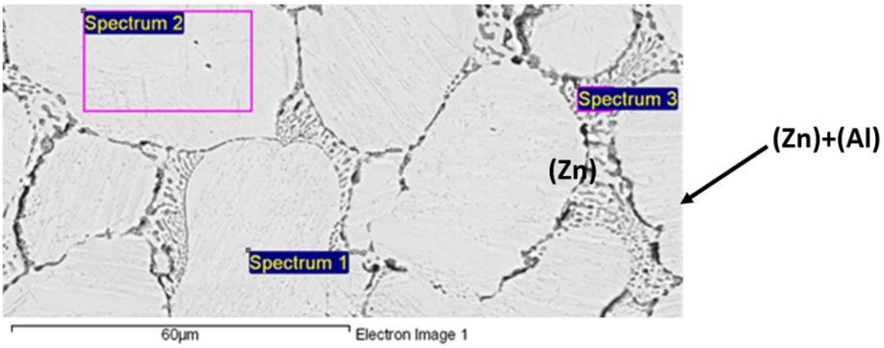


Figure 5
Binary Al-Zn diagram [7]



Spectrum	Al wt. %	Zn wt. %
Spectrum 1	1.10	98.90
Spectrum 2	1.32	98.68
Spectrum 3	16.53	83.47

Figure 6
Microstructure of Zn4Al solder

The ZnAl4 solder shows a narrower fusion interval, while it is of close-to eutectic composition. By the DSC analysis (Fig. 7a), a temperature of 277.6°C starts the onset of eutectoid transformation. The following reaction takes place at this temperature: Alrichfcc + hcp (Zn) / Zn-richfcc. The eutectic (Zn + 6 wt.% Al), segregated along the grain boundaries of Zn matrix of the solder starts to melt at 380.7°C. The solid solution (Zn) attains its fully liquid state at 385.9°C – Fig. 7b.

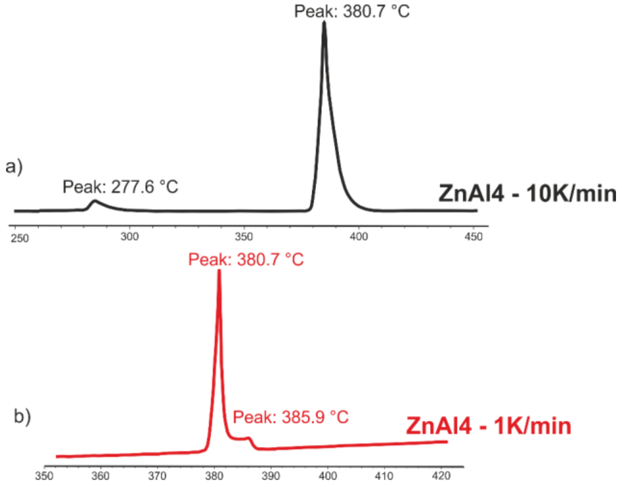


Figure 7
DSC analysis of Zn-4Al solder at heating rate: a) 10K/min b)1K/min

Mechanical tests of type Zn-Al solders were performed. The dimensions of test pieces were designed and calculated. Fig. 8 shows the dimensions of test specimens and the actual test piece. Three pieces for each type of alloy were used for experimental assessment. The results of tensile strength tests of soldered type Zn-Al alloys are documented in Fig. 9.

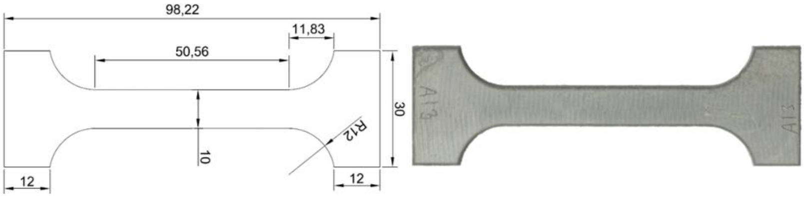


Figure 8

Dimensions of test specimen and a real view on a specimen of Zn4Al solder

Figure 9

Tensile strength of soldered alloys type Zn-Al in dependence on Al content

Generally, Al content slightly increases the strength of Zn-Al solder. By increasing Al content, the strength of Zn-Al solder increases – Fig. 15. The variance in tensile strength between ZnAl1 and ZnAl4 solder is around 35 MPa.

Analysis of Joints in Al_2O_3 and SiC Ceramic Materials Soldered with Zn4Al

Fig. 10 shows the difference in the transition zone of Al_2O_3/Zn4Al and SiC/Zn4Al joints. A wide transition zone up to 70 μm in width was formed on the boundary with SiC, where an increased amount, mainly of carbidic and silicon particles, was identified. Due to ultrasound erosion, the solder penetrated the grains of the ceramic materials and carbidic particles from ceramics and silicon particles, infiltrated in the grain boundaries of SiC ceramics and displaced into the solder. The concentration profiles in the SiC/Zn4Al boundary zone are shown in Fig. 11.

No distinct transition layer is observable in the boundary with Al_2O_3 ceramics – Fig. 10b. The character of solder matrix in this boundary remains unchanged. No new transition phases were identified. The bond with Al_2O_3 ceramics is formed by solder adhesion with Al_2O_3 ceramics.

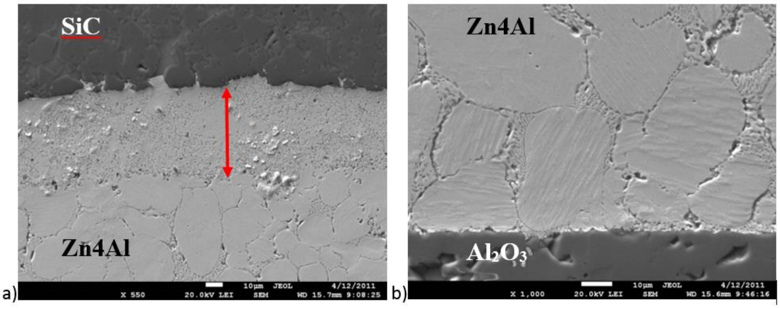


Figure 10

Microstructure in the boundary of a) SiC/Zn4Al, b)Al_2O_3/Zn4Al bonds

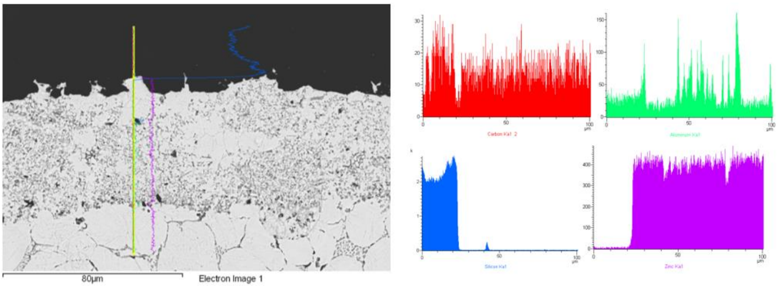


Figure 11

Microstructure in the boundary of SiC/Zn4Al bond and the concentration profiles of C, Al, Si and Zn elements

Analysis of Bond between Cu and Zn4Al Solder

A wide zone of two new intermetallic phases was formed in the boundary of the Cu/Zn4Al/Cu bond (Fig. 12). The $CuZn_4$ and Cu_5Zn_8 phases were identified. The concentration profiles of Cu, Zn and Al elements are shown in Fig. 13.

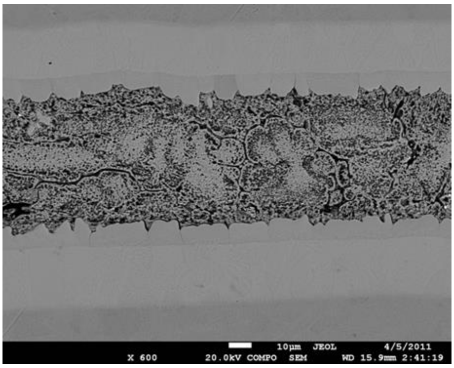


Figure 12

Microstructure of Cu/Zn4Al/Cu bond boundary

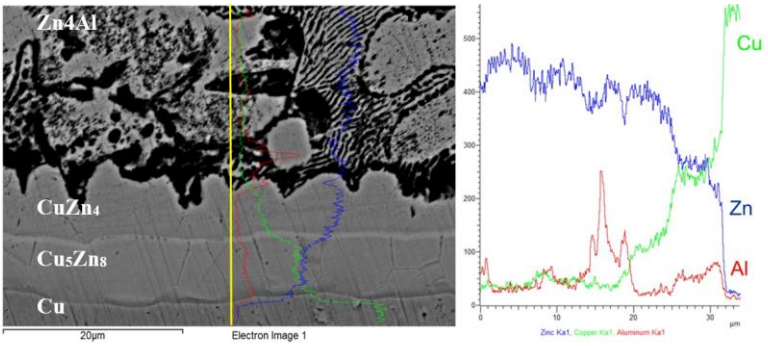


Figure 13
Line EDX analysis of Cu/Zn4Al soldered joint and concentration profiles of Cu, Zn, Al elements in Cu/Zn4Al boundary

The Results of Shear Strength of Soldered Joints

Research within this study was primary oriented toward soldering Al_2O_3 and SiC ceramic substrates and Cu substrates. The experiments to determine the shear strength of soldered joints were also extended to other metallic materials such as Al, Ni, Ti and CrNi steel, in order to prove the wider applicability of Zn4Al solder.

Measurement was performed on 4 specimens of each material. The results of average shear strength of joints are documented in Fig. 14. The shear strength of Al_2O_3 ceramics attained 81.0 MPa. With SiC ceramics, a slightly lower strength of 65.0 MPa was observed. With the copper substrate, a shear strength of 84.0 MPa was measured. The highest shear strength was achieved with aluminum -- 174.5 MPa.

For a more exact identification fractured surfaces in the boundary of Cu/Zn4Al and eventually Al_2O_3/Zn4Al bonds were also identified (Figs. 15, 16).

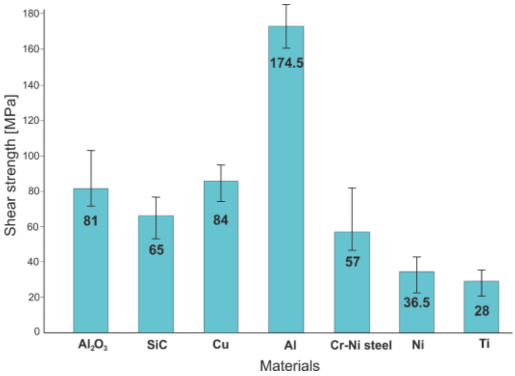


Figure 14
The results of shear strength measurements in joints fabricated by use of Zn4Al solder

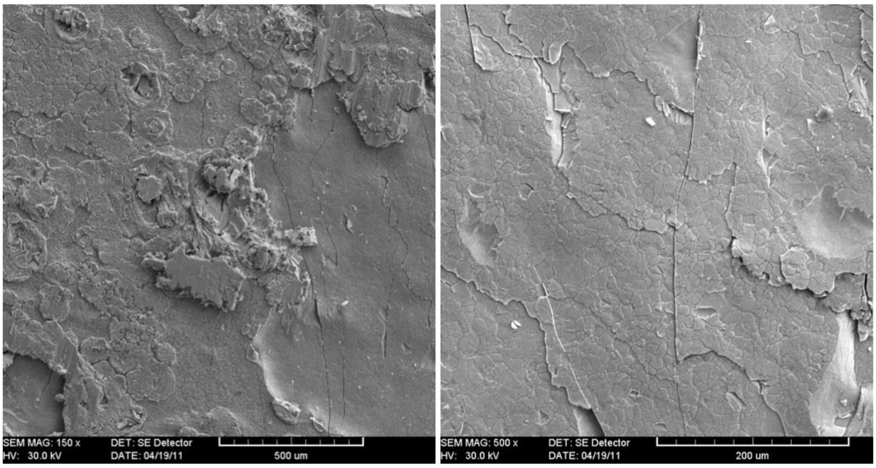


Figure 15
Fractured surface of Zn4Al/Cu joint

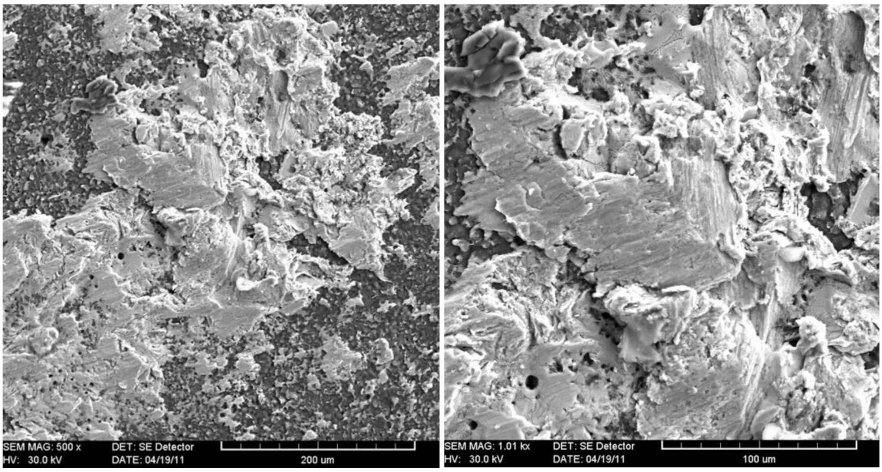


Figure 16
Fractured surface of Zn4Al/Al_2O_3 joint

Formation of a typical ductile failure by shear mechanism was documented in Cu/Zn4Al bond (Fig. 15). Fig. 16 shows the fractured surfaces of Al_2O_3/Zn4Al bonds. Fracture morphology evidently shows a visible motion of the shearing tool with a ductile fracture.

After the shear test, 100% coverage of Cu substrate with Zn4Al solder remained. To the contrary, in the case of Cu substrate the solder was detached from the ceramic substrate. Partial coverage of Al_2O_3 substrate was observed, as documented in Fig. 16.

4 Discussion

The results achieved by direct bonding of ceramic and metallic materials proved that Zn-based solder ensures the wettability at application of ultrasound activation, by which the Zn4Al solder becomes suitable for practical soldering applications.

For a comparison of results from the shear strength measurement we also present the results from similar studies, while it should be taken into account that different works make use of different test methods, the shape of test pieces and loading rates during testing. They also use different compositions of soldering alloys and soldering parameters.

For example in the case of the application of Zn-Al (Zn14Al) solders in work [8], with Al_2O_3/Zn14Al/Cu bonds, a shear strength of 80 MPa was observed at ultrasound power of 200 W. In study [1], the joint of SiC ceramic substrate, soldered with Zn8.5Al1Mg solder, attained a shear strength of 148.1 MPa at 8s. of ultrasound action.

In study [2], sapphire was soldered with ultrasound activation by use of Sn10Zn2Al solder. The shear strength of joints attained 43 to 48 MPa. More studies dealt with Sn-Ag-Ti solders. Also, new metallic, ceramic and non-metallic materials were tested.

For example in study [3], the Al_2O_3/Sn-Ag-Ti/Al_2O_3 bond showed a shear strength of 24 MPa. In work [4], the following strengths were achieved by soldering: Cu/Cu (14.3MPa), ITO/ITO (6.8 MPa) and ITO/Cu (3.4 MPa). Similarly, in study [8], the attained shear strengths of joints were as follows: alumina/alumina (13.5 MPa), copper/copper (14.3 MPa) and alumina/copper (10.2 MPa).

Conclusions

The aim of work was oriented toward the direct bonding of Al_2O_3, SiC ceramic substrates and a copper substrate. We examined the behavior of Zn-based solder, alloyed with Al, for the wetting of Al_2O_3 ceramics and other ceramic materials and the formation of a strong bond with them. Due to this, several analyses of the transition zones for the bonds and the measurements of shear strengths were performed. The following results were achieved:

- DSC analysis revealed that the solder has a smaller melting interval. At a temperature of 380.7°C, the eutecticum (Zn + 6wt% Al) segregated along the zinc matrix of the solder starts to melt. The solid solution (Zn) attains a fully liquid state at 385.9°C
- The matrix of Zn4Al solder is formed of great grains of solid solution (Zn) with a Zn concentration of 98.68 wt%. A fine eutecticum, formed of solid solutions (Zn) + (Al), is segregated along the grain boundaries.

- In SiC/Zn4Al bond boundary a transition zone was formed up to 70 μm in width, where increased amounts, mainly of carbidic and silicon particles, were identified.
- No distinct transition layer was observed in the Al_2O_3/Zn4Al bond boundary. The character of solder matrix in this boundary is unchanged. The Al_2O_3/Zn4Al bond is formed due to the adhesion of solder with Al_2O_3 ceramics.
- A wide zone of two new intermetallic phases was formed on the Cu/Zn4Al boundary (Fig. 14), where $CuZn_4$ and Cu_5Zn_8 phases were identified.
- The shear strength of 81.0 MPa was obtained with Al_2O_3 ceramics. With SiC ceramics, a slightly lower strength of 65.0 MPa was observed. With copper substrate, a shear strength of 84.0 MPa was measured. The highest shear strength was achieved with aluminum at 174.5 MPa.

After the shear test, 100% coverage of Cu substrate with Zn4Al solder remained. In contrast, for the case of the Cu substrate, the solder was detached from the ceramic substrate, whereas, partial coverage of Al_2O_3 substrate was observed.

Acknowledgement

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References

[1] Chen, X., Yan, J., Ren, S., et al., Microstructure, Mechanical Properties, and Bonding Mechanism of Ultrasonic-assisted Brazed Joints of SiC Ceramics with ZnAlMg Filler Metals in Air. In *Ceramics International*, Vol. 40, 2014, pp. 683-689

[2] Cui, W., Yan, J., Dai, Y., Li, D., Building a Nano-Crystalline α-alumina Layer at a Liquid Metal/Sapphire Interface by Ultrasound. In *Ultrasonics Sonochemistry*, Vol. 22, 2015, pp. 108-112

[3] Koleňák, R., Šebo, P., Provazník, M., Koleňáková, M., Ulrich, K. Shear Strength and Wettability of Active Sn3.5Ag4Ti(Ce,Ga) Solder on Al_2O_3 Ceramics. In *Materials and Design*, Vol. 32, 2011, pp. 3997-4003

[4] Chang, S. Y., Tsao, L. C., Chiang, M. J., et al., Active Soldering of Indium Tin Oxide (ITO) With Cu in Air Using an Sn3.5Ag4Ti(Ce,Ga) Filler. In *Journal of Materials Engineering and Performance*, Vol. 12, No. 4, 2003, pp. 383-390

[5] Chang, S. Y., Chuang, T. H., Yang, C. L., Low Temperature Bonding of Alumina/Alumina and Alumina/Copper in Air Using Sn3.5Ag4Ti(Ce,Ga) Filler. In *Journal of Electronic Materials*, Vol. 36, No. 9, 2007, pp. 1193-1199

[6] M. Martinkovič [patent inventor], R. Koleňák [patent inventor]: The Form on the Production of Experimental Soldered Joint – Patent 288180. Industrial Property Office of the Slovak Republic [patentee]. Date of patent accordance: 12.02.2014

[7] Murray, J. L. The Al-Zn (Aluminium-Zinc) System. In Bulletin of Alloy Phase Diagrams, Vol. 4, Is. 1, 1983, pp. 55-73

[8] Ji, H., Chen, H., Li, M., Microstructures and Properties of Alumina/Copper Joints Fabricated by Ultrasonic-assisted Brazing for Replacing DBC in Power Electronics Packaging. In 15th International Conference on Electronic Packaging Technology, IEEE, 2014, pp. 1291-1295