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Soldering of Copper with High-Temperature Zn-Based Solders

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Abstract

The work deals with the study of interaction Cu substrate (purity 5N) and Zn4Al and Zn6Al6Ag (purity 4N) solders for higher application temperatures. Soldering was performed with power ultrasound in the air without flux application at temperature 420 °C. Acting time of ultrasonic vibration was 5 s. Soldered joints were assessed by optical light microscopy, EDX microanalysis and DSC analysis. It was found out that the melting temperatures of solders were 404.9 °C and 396.9 °C. Intermetallic layers (IM) $CuZn_4$ and Cu_5Zn_8 were formed at the Cu/Zn4Al boundary. At the boundary Cu/Zn6Al6Ag there were formed $AgZn_3$ and Cu_5Zn_8 IM layers. Shear strength of joint Cu/Zn4Al was 34.5 MPa and shear strength of Cu/Zn6Al6Ag was 39 MPa.

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Keywords: Zinc solders; ultrasonic soldering; copper; DSC analysis; shear strength

1. Introduction

Nowadays soldering by higher application temperatures is key technology for electronic components and its assembly. High-temperature solders have been widely used in various types of applications not only as die-attach solders but also for assembling optical components, automobile circuit boards, circuit modules for step soldering, etc. These technologies can provide value-added characteristics to the products, including excellent heat conductivity, electric conductivity and high reliability of soldered joints [1]. Appearance of lead-free alternative for high-lead solder Pb-Sn is the main objective in recent years due to EU directive [2].

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Authors [3] have studied the high-frequency induction soldering of the magnesium alloy AZ31B by Zn49Mg solder. Melting range of this solder was from 334 to 352 °C. Diffusion zone with width 40 µm was formed after soldering [3]. For soldering on the same substrate was used Zn19Al solder too. Temperature of solidus and liquidus of this solder were 389, respectively 447 °C. Boundary of joint consisted of solid solution α-Mg and eutectoid structure MgZn [4].

Authors [5] soldered Cu substrate by Zn4Al3Mg3Ga solder. Temperature of soldering was in the range from 370 to 400 °C. After analysis of soldered joint it was found out that the boundary formed $CuZn_4$, Cu_5Zn_8 a CuZn IM layers [5]. Formation of these layers was confirmed in the other study too [6]. Authors used the same Zn4Al3Mg3Ga solder for soldering Ni metallized Cu substrate. In this case no IM layer was observed at the solder/substrate interface. Wettability on Ni metallized Cu substrate was lower as compared to that at bare Cu substrate. Shear strength was found to be higher on bare Cu substrate (24.2 MPa) as compared to Ni metallized Cu substrate (20.5 MPa). Shear strength of standard Pb5Sn solder was also measured for comparison and found to be 28.2 MPa [7].

The solder Zn(4-6)Al(1-5)Cu for higher application temperatures was designed to has a melting range between 382 and 402 °C. The raising Al content improved the spreadability and electrical resistivity. The alloying contents increased hardness and tensile strength of solder. Addition of 1 wt. % Cu to ZnAl4 solder in case of soldering on Cu substrate resulted in reduction of activation energy for growth of intermetallic compounds [8]. Also another authors studied solders for higher application temperatures [9, 10, 11,12,13].

Presented work describes realisation of ultrasonic soldering of Cu substrate with zinc solders for higher application temperatures. Soldering was performed on air, without using a flux with heating by hot plate. The aim of study was to investigate the interaction between zinc solders and copper substrate, determinate properties of solders and shear strength of soldered joints.

2. Experimental

Selected zinc based solders Zn4Al and Zn6Al6Ag had 4N purity. Solder Zn4Al contains 4 wt. % of Al and solder Zn6Al6Ag contains 6 wt. % of Al and 6 wt. % of Ag. As substrate, Cu with 5N (99.999 %) purity and diameter Ø 15 mm and thickness 2 mm was used on soldering. Schemes of created joints are in the fig. 1.

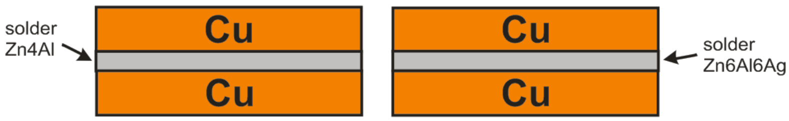

Fig. 1. Schemes of soldered joints.

Soldering process took place by mechanical activation of solder by ultrasound in the air. Soldering temperature was selected 20 °C above the liquidus of corresponding solder. Acting time of ultrasonic vibration was 5 s and ultrasonic frequency was 40 kHz. Heating of specimens was ensured by a hot plate method with temperature control by use of NiCr/NiSi thermocouple. Plate was heated by electric resistance with working temperature control. Ultrasonic device with 40 kHz frequency and 400 W output power was used for creating of joints (fig. 1). Device consists of a generator and ultrasonic head. The head is constructed of a piezoelectric transducer and a sonotrode made of Ti.

After soldering, the specimens were prepared by a standard metallographic procedure of grinding on SiC emery papers and polished on disks with diamond pastes with 9, 6, 3 and 1 µm grain size. Specimens were observed on light optical microscope type NEOPHOT 32. Light optical microscopy provided information about the size, amount and distribution of phases which were formed after soldering on solder/substrate boundary.

EDX analysis was used for determination of chemical composition, concentration of individual elements and identification of reaction products. It was performed on equipment energy-dispersive X-ray spectroscopy analyser, which was a part of electron scanning microscope type JEOL JXA-840A.

Differential scanning calorimetry (DSC analysis) was used for measurement melting temperature range of solders. DSC analysis was performed on NETZSCH STA 409 CD device with the evaluating software NETZSCH Proteus. Temperature of heating was 10 °C/min in the Ar protecting atmosphere.

Shear test on universal tear device LabTest 5.250Sp1-VM was performed for determination of shear strength. Developed shear jig was used for change direction of application of tensile axial loading force on test sample. This jig secured uniform load of sample by shearing in the plain of solder/substrate border line. At the sample production holding time on the soldering temperature was 30 s and the time of ultrasound activation was 5 s. Five samples of each combination was produced for determination of shear strength of soldered joints Cu/Zn4Al and Cu/Zn6Al6Ag. Final value of shear strength was arithmetic average of these measurements.

3. Experimental results

Exact melting temperatures of solders were determined by DSC analysis. By these results, temperature of soldering was defined on 20 °C above liquidus of relevant solder. Solder Zn4Al has a wide melting range. Eutectoid transformation begins at temperature 282.5 °C, what is expecting from Zn-Al binary diagram. Eutectic phases of all solders start melting at temperature 381.4 °C. Complete melting of Zn4Al solder is achieved at temperature 408.6 °C. The next analysed solder was Zn6Al6Ag solder (fig. 2). Complete melting of this solder is achieved at 399.9 °C. At this moment entire volume of solder was melted. The first peak on DSC curve (293.9 °C) notice a eutectoid transformation. Start of solder melting is at temperature 386.8 °C. Results of DSC analysis are summarized in the table 1.

Table 1. Final values of melting temperatures of zinc solders.

Solder	Zn4Al	Zn6Ag6Al
Heating rate [K/min]	10	10
Temp. range of measurement [°C]	250-450	200-450
Onset temperature [°C]	381.4	386.8
Peak temperature [°C]	404.9	396.9
End temperature [°C]	408.6	399.9

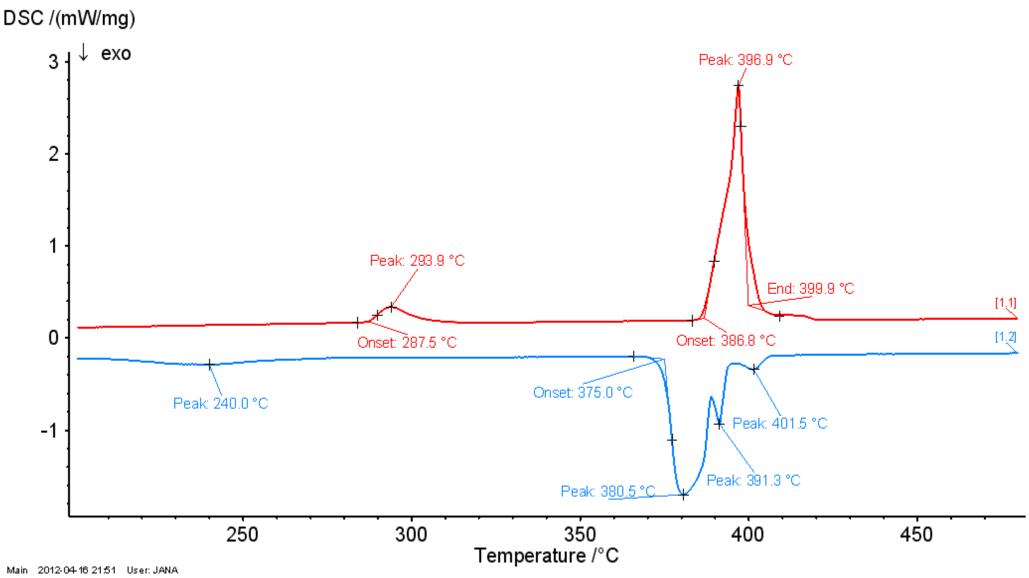

Fig. 2. DSC analysis of Zn6Al6Ag solder.

Microstructure of Zn4Al solder consist of βZn primary solid solution and a lamellar eutectic Zn-Al structure. On the solder/substrate boundary there was formed transition zone by dissolving a Cu substrate in the solder. Copper diffuses to the solder and forms IM phases inside the joint too. From quantitative analysis, binary diagrams and by calculation using the Thermo-Calc software it was found, that boundary is creating by Cu_5Zn_8 phase (from substrate side) and $CuZn_4$ phase (from solder side).

Microstructure of Zn6Al6Ag solder consist of βZn solid solutions, eutectic Zn-Al structure and $AgZn_3$ phase. In comparison with Zn4Al/Cu joint we can observe higher volume of phases inside the joint and even bigger thickness of these phases on boundary. It is caused by addition of next element - Ag to the composition of solder. According XRD analysis silver together with the zinc creates an $AgZn_3$ phase. This phase and Cu_5Zn_8 phase created a boundary of this Cu/Zn6Al6Ag joint.

By the application of ultrasound energy both solders wetted Cu substrate and created a joint. Joints were compact, without cracks, cavities or discontinuities.

Fig. 3 shows a concentration profiles of Zn, Al and Cu elements on Cu/Zn4Al solder boundary. We can observed a formation of Cu_5Zn_8 a $CuZn_4$ IM layers on the boundary.

EDX mapping of soldered joint Cu/Zn6Al6Ag - fig. 4 confirms that there is an interaction of solder elements with Cu substrate. Elements mapping shows a formation of $AgZn_3$ IM layer on solder/substrate boundary. $AgZn_3$ layer is formed from solder side and Cu_5Zn_8 from substrate side. Aluminium fills dark areas in the solder matrix.

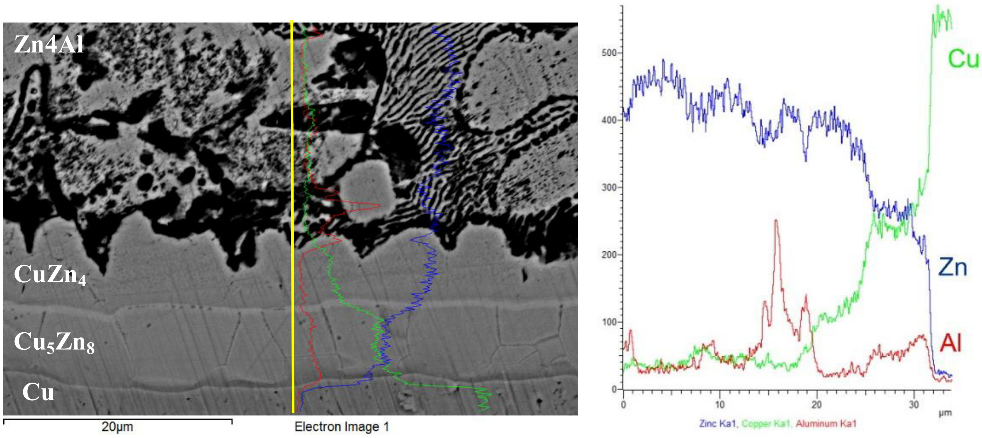

Fig. 3. Line EDX analysis of Cu/Zn4Al soldered joint and concentration profiles of Cu, Zn, Al elements on Cu/Zn4Al boundary.

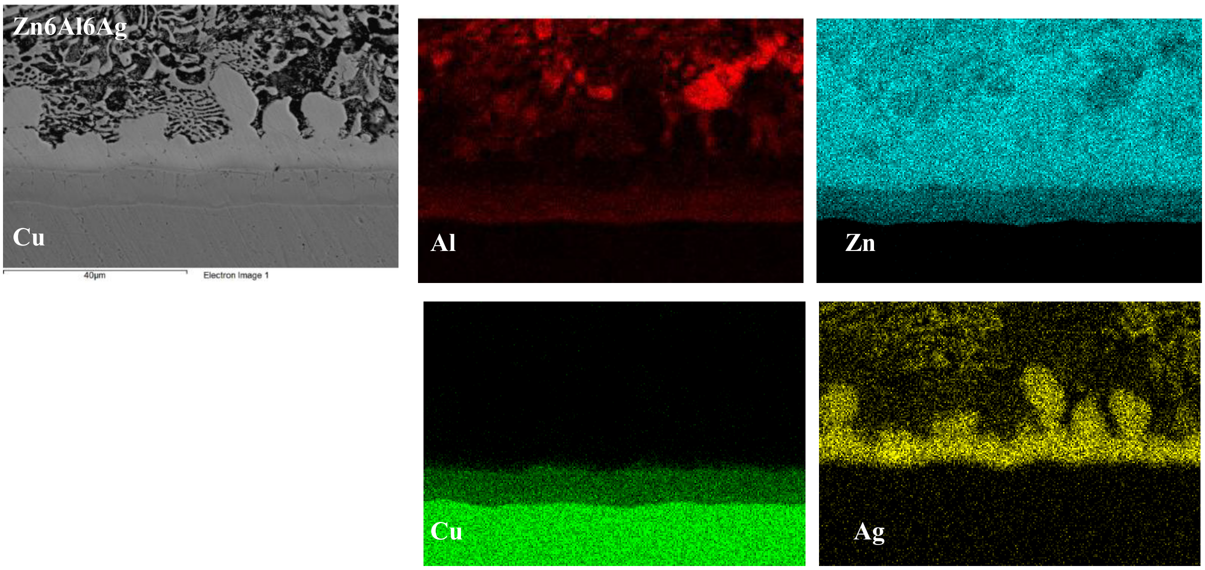

Fig. 4. Planar distribution of elements on the Cu/Zn6Al6Ag boundary.

Shear test was performed for determination of shear strength of soldered joints. Soldered joints with the Zn4Al solder has average strength 34.5 MPa. Joints with Zn6Al6Ag solder has strength 39 MPa. Results of shear test are in the fig. 5.

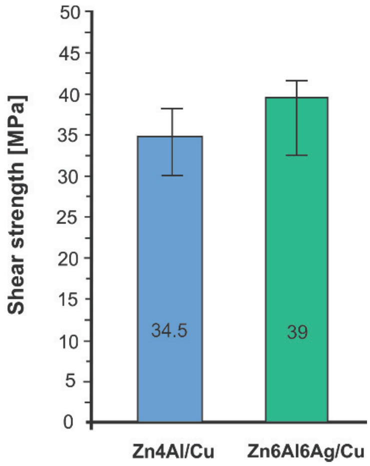

Fig. 5. Shear strength of soldered joints with solders Zn4Al a Zn6Al6Ag.

Conclusion

Lead-free solder alternative is looking for in this area of research. By this reason Zn-based alternatives are introduced in this article with their soldering and mechanical properties. Presented work dealt with fluxless ultrasonic soldering of copper substrate in the air by zinc solders for higher application temperatures. Acting time of ultrasonic vibration was 2 s and ultrasonic frequency was 40 kHz. Soldering temperature was chosen 20 °C above liquidus of relevant solder. The Zn4Al, Zn6Al6Ag solders were prepared from high purity materials (4N) and Cu substrate had purity 5N. Joints made by ultrasonic soldering were compact, without cracks, cavities or discontinuities.
Finally, the following significant pieces of knowledge may be summarised:

- Melting temperatures were determined by DSC analysis. Melting temperatures of Zn4Al, Zn6Al6Ag solders were 404.9 °C and 396.9 °C. Soldering temperature can be thereafter selected according of these results.
- Microstructure of Zn4Al solder consist of βZn primary solid solution and a lamellar eutectic Zn-Al structure. Microstructure of Zn6Al6Ag solder consist of βZn solid solutions, eutectic Zn-Al structure and $AgZn_3$ phase.
- On the solder/Cu substrate boundary there was formed evident transition zone by dissolving a Cu substrate in the solder. The boundary Cu/Zn4Al was creating by Cu_5Zn_8 phase from substrate side and $CuZn_4$ phase from solder side. The boundary Cu/Zn6Al6Ag was creating by $AgZn_3$ a Cu_5Zn_8 phases.
- Shear strength of soldered joints was 34.5 MPa (Zn4Al/Cu joint) and 39 MPa (Zn6Al6Ag/Cu joint).

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