

**RESEARCH OF INTERACTION BETWEEN Zn BASED SOLDERS
AND Cu, Al SUBSTRATES**

Michal PRACH, Igor KOSTOLNÝ, Roman KOLEŇÁK

Abstract

The paper deals with the study of interaction between Cu, Al substrates (purity 5N) and ZnAl₄, ZnAg₆Al₆ zinc 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 3 s and ultrasound frequency was 40 kHz. Soldered joints were assessed by optical light microscopy and EDX microanalysis. Intermetallic layers (IM) CuZn₄ and Cu₅Zn₈ were formed at the Cu/ZnAl₄ boundary. The βZn-αAl mechanical mixture was formed at the Al/ZnAl₄ boundary. AgZn₃ and Cu₅Zn₈ IM layers were formed at the Cu/ZnAg₆Al₆ boundary, and mechanical mixture of βZn-αAl and AgZn₃ intermetallic mixture were formed at the boundary Al/ZnAg₆Al₆.

Key words

zinc solders, ultrasonic soldering, copper, aluminium, higher application temperatures

INTRODUCTION

Nowadays, soldering by higher application temperatures is the key technology for electronic components and their 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 (Suganuma 2009). Appearance of lead-free alternative for high-lead Pb-Sn solder is the main objective in the recent years according to the EU directive (Kroupa 2012).

Authors (Ma 2013) have studied the high-frequency induction soldering of the AZ31B magnesium alloy by Zn₄₉Mg solder. Melting range of this solder was from 334 to 352 °C.

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Diffusion zone with width 40 μm was formed after soldering (Ma 2013). For soldering the same substrate, Zn19Al solder was used, too. Temperatures of solidus and liquidus of this solder were 389, respectively 447 $^{\circ}\text{C}$. Boundary of joint consisted of α -Mg solid solution and MgZn eutectoid structure (Ma 2010).

Authors (Haque 2012) soldered Cu substrate by ZnAl43Mg3Ga solder. Temperature of soldering was in the range 370 - 400 $^{\circ}\text{C}$. After analysis of soldered joint, it was found that the boundary was formed by the CuZn_4 , Cu_5Zn_8 and CuZn IM layers (Haque 2012). Formation of these layers was confirmed in another study, too (Takaku 2008). Authors used the same ZnAl43Mg3Ga solder for soldering Ni metallized Cu substrate. In this case, no IM layer was observed at the solder/substrate interface. Wetting on Ni metallized Cu substrate was found to be 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 (Haque 2010).

Authors (Li 2011, Xiao 2013) have studied the microstructure and mechanical properties of joints by application of ZnAl5 and ZnAl3 solders. Removal of surface oxides was performed with the aid of ultrasonic energy. The Al 2024/ZnAl5/Al 2024 joints were fabricated at soldering temperature 400 $^{\circ}\text{C}$. By prolonging the time of ultrasonic vibrations from 3 to 30s, a drop in the volume of fine eutectic phases from 12.9 % to 0.9 % was observed, and also tensile strength increased from 149 up to 153 MPa. The Al 1060/ZnAl3/Cu joints were fabricated at soldering temperature 400 to 480 $^{\circ}\text{C}$. Formation of $\text{Al}_{4,2}\text{Cu}_{3,2}\text{Zn}_{0,7}$ intermetallic phase with the lowest thickness 1.9 μm was observed at soldering temperature 440 $^{\circ}\text{C}$. The highest tensile strength measured at this temperature was 78.93 MPa.

Presented paper describes the implementation of ultrasonic soldering of the Cu and Al substrates by 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 investigation of interaction between solders and the Cu or Al substrate. Zinc solders ZnAl4 and ZnAg6Al6 were used in experiments. Other studies with these solders were performed by the authors (Koleňák 2014, Prach 2014).

EXPERIMENTAL

Aluminium with 4N purity and copper with 5N purity in the form of rolled sheet in thickness 1.5 mm was used for soldering. Substrates for soldering were cut by water jet to the circular shape with diameter \varnothing 15 mm. The selected zinc-based ZnAl4 and ZnAg6Al6 solders had 4N purity. Their chemical composition is given in Table 1.

CHEMICAL COMPOSITION OF ZnAl4 AND ZnAg6Al6 SOLDERS Table 1

Composition [wt. %]	Zn	Al	Ag
ZnAl4	96	4	-
ZnAg6Al6	88	6	6

Soldering process took place by mechanical activation of solder by ultrasound in the air. Removal of surface oxides was ensured by application of ultrasound. Soldering temperature was selected at 420 $^{\circ}\text{C}$. Acting time of ultrasonic vibration was 3s and ultrasonic frequency was 40 kHz. Heating of specimens was ensured by a hot plate method with temperature control by the 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 fabricating joints (Fig. 1). The device consists of a generator and ultrasonic head. The head is constructed of a piezoelectric transducer and a sonotrode made of Ti. The scheme of ultrasonic activation is shown in Fig. 2.

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 of NEOPHOT 32 type. Light optical microscopy provided information about the size, amount and distribution of phases which were formed after soldering on the solder/substrate boundary.

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

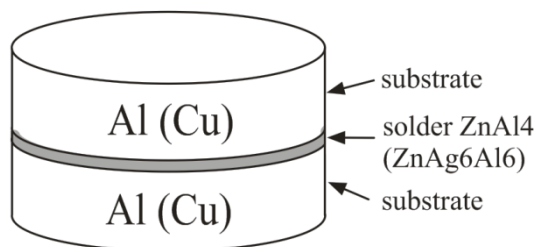


Fig. 1 Test specimen

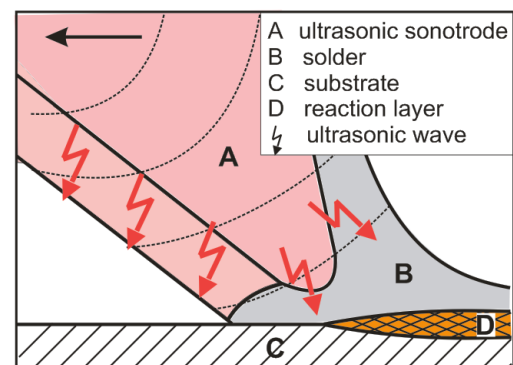


Fig. 2 Scheme of ultrasonic activation (Hillen 2000)

EXPERIMENTAL RESULTS

Microstructure of ZnAl4 solder consists of β -Zn primary solid solution and a lamellar eutectic Zn-Al structure. Microstructure of ZnAg6Al6 solder consists of α -Al, β -Zn solid solutions and AgZn₃ phase. X-ray diffraction (XRD analysis) proved the presence of α -Al, β -Zn solid solutions and AgZn₃ phase.

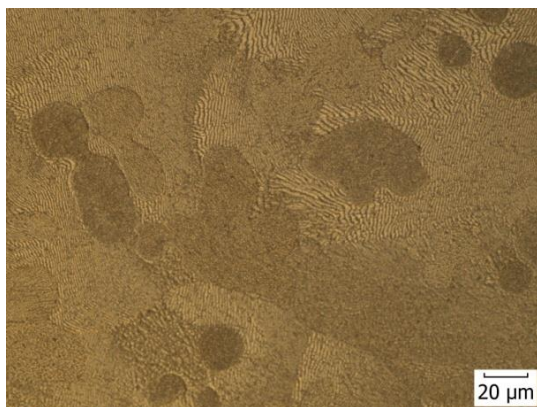


Fig. 3 Microstructure of ZnAl4 solder

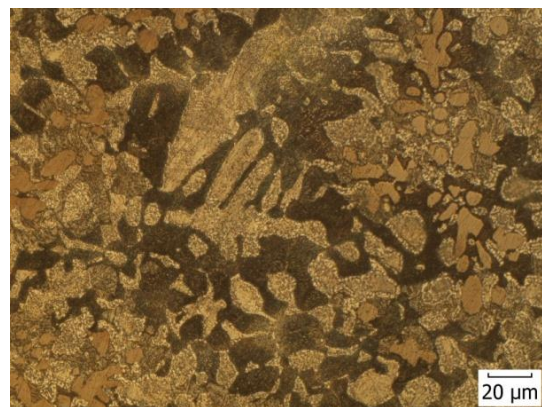


Fig. 4 Microstructure of ZnAg6Al6 solder

By the application of ultrasound energy, the ZnAl4 and ZnAg6Al6 solders wetted the Cu and Al substrate and formed joints. The joints were compact, without cracks, cavities or discontinuities. Erosive activity owing to the effect of ultrasound resulted in the formation of

an undulated boundary in the zone of all metallurgical joints. Example of undulated boundary of Al/ZnAl4/Al joint is in the Fig. 5. Arrows pointed the erosion of substrate caused by the effect of ultrasound activation.

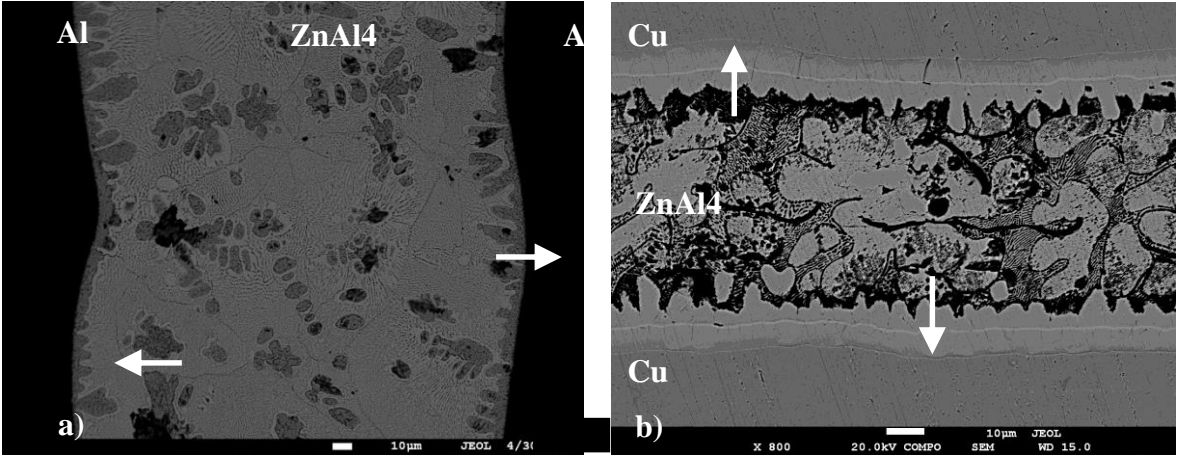


Fig. 5 Microstructure of soldered joint a) Al/ZnAl4/Al, b) Cu/ZnAl4/Cu

Fig. 4 shows the microstructure of soldered joint formed of Al substrate and ZnAl4 solder. Transition zone was formed on the boundary. Measured average width of diffusion zone was 12.8 μm. Microstructure of Cu/ZnAl4 soldered joint is in Fig. 5. On the solder/substrate boundary, evident transition zone was formed by dissolving the Cu substrate in the solder. As we can see in Fig. 5, Cu diffuses to the solder and forms IM phases inside the joint, too. From quantitative analysis, modelling in ThermoCalc software and binary diagrams, it was found that boundary is formed of Cu₅Zn₈ phase (from substrate side) and CuZn₄ phase (from solder side).



Fig. 4 Microstructure of Al/ZnAl4 soldered joint

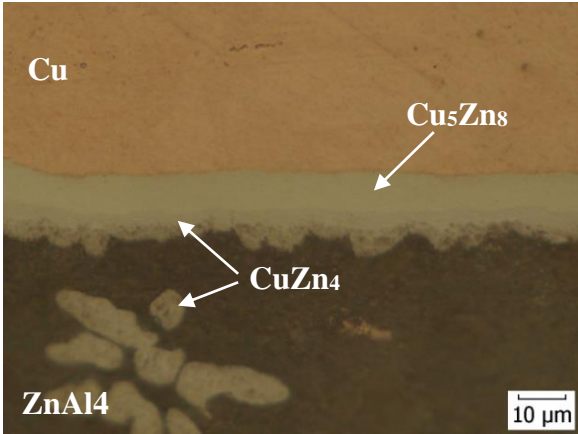


Fig. 5 Microstructure of Cu/ZnAl4/Cu soldered joint

Fig. 6 shows concentration profiles of the Zn, Al and Ag elements on the Al/ZnAg6Al6 solder boundary. On the solder/substrate boundary, a transition zone was formed. According to concentration profiles, it is obvious that concentration on the boundary goes down sharply. This zone is formed by the mechanical mixture of βZn-αAl and AgZn₃ intermetallic mixture. Concentration profiles of elements at the ZnAg6Al6/Cu joint are in Fig. 7.

Line EDX analysis of Cu/ZnAg6Al6 joint confirms that there is an interaction of solder elements with the Cu substrate. Concentration profiles show a formation of Cu₅Zn₈ IM layer on the solder/substrate boundary. The AgZn₃ layer is formed on the solder side. Aluminium has an increased concentration in the solder volume - dark areas.

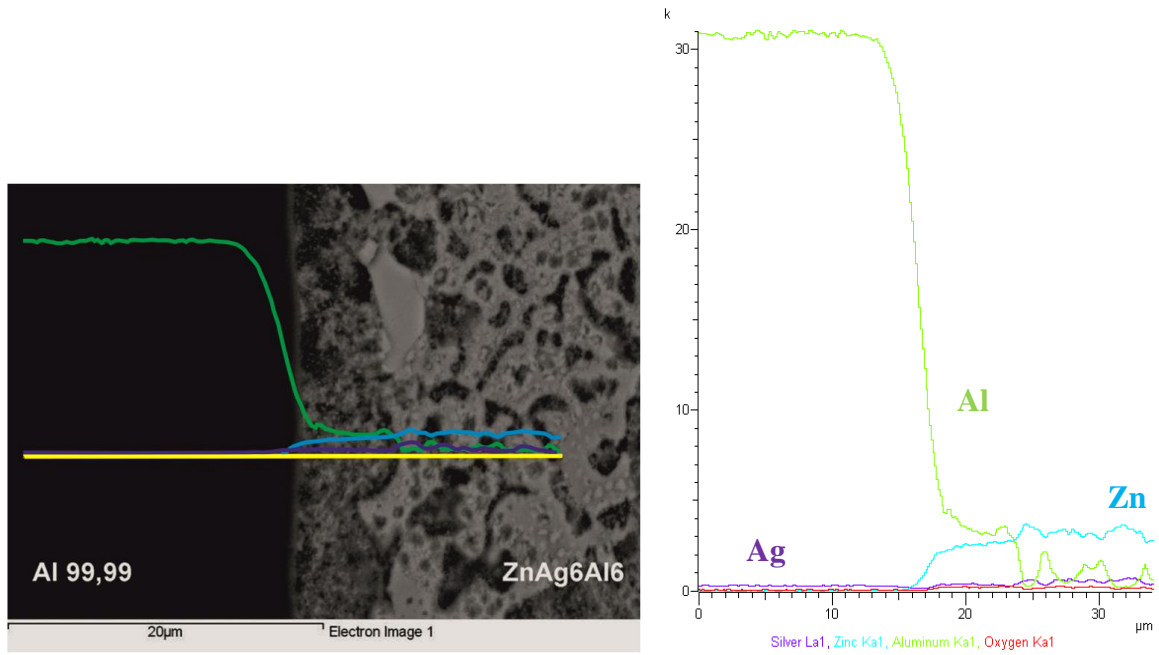


Fig. 6 Line EDX analysis of Al/ZnAg6Al6 soldered joint and concentration profiles of Cu, Zn, Al elements on Cu/ZnAl4 boundary

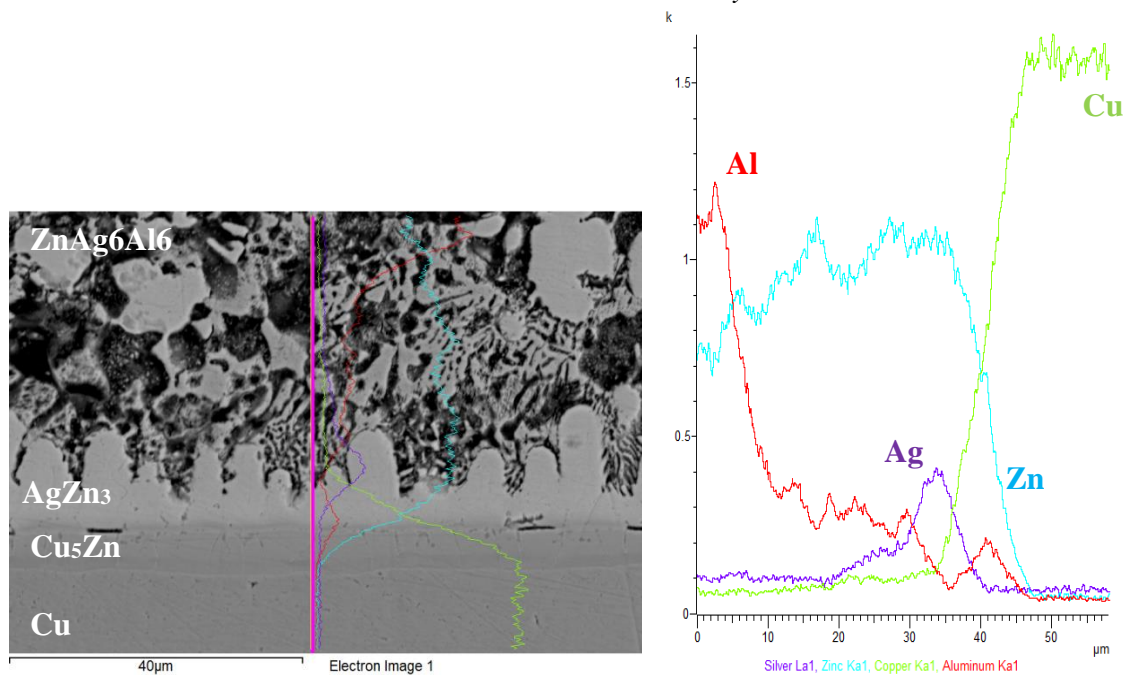


Fig. 7 Line EDX analysis of Cu/ZnAg6Al6 soldered joint and concentration profiles of Ag, Zn, Cu, Al elements on Cu/ZnAg6Al6 boundary

CONCLUSION

Presented paper dealt with fluxless ultrasonic soldering of copper and aluminium substrate in the air by zinc solders for higher application temperatures. The ZnAl4 and ZnAg6Al6 solders were prepared from the high purity materials 4N. Acting time of ultrasonic vibration was 3s and ultrasonic frequency was 40 kHz. Soldering temperature was chosen at 420 °C. The structure of joints was studied by the use of light microscopy and EDX microanalysis.

Based on the achieved results, the following was observed:

- ZnAl4 solder is composed of β Zn solid solution and lamellar eutectic Zn-Al structure;
- ZnAg6Al6 solder consists of α Al, β Zn solid solutions and AgZn₃ phase;
- ZnAl4 solder formed β Zn- α Al mechanical mixture on the boundary with Al substrate;
- Mechanical mixture of β Zn- α Al and AgZn₃ intermetallic mixture were identified on the Al/ZnAg6Al6 joint boundary;
- On the solder/Cu substrate boundary, evident transition zone was formed by dissolving the Cu substrate in the solder. The Cu/Zn4Al boundary was formed by the Cu₅Zn₈ phase on the substrate side and the CuZn₄ phase on the solder side.
- The Cu/ZnAg6Al6 boundary was formed by the AgZn₃ and Cu₅Zn₈ phases;
- Owing to erosive activity of ultrasound, an undulated boundary was observed in case of both joints;
- The obtained results indicate that the examined zinc solders are more suitable for soldering copper substrate due to the stronger interaction on joint boundary.

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