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R. KOLEŇÁK*, M. MARTINKOVIČ*, M. KOLEŇÁKOVÁ*

# SHEAR STRENGTH AND DSC ANALYSIS OF HIGH-TEMPERATURE SOLDERS

# WYTRZYMAŁOŚĆ NA ŚCINANIE I ANALIZA DSC WYSOKOTEMPERATUROWYCH STOPÓW LUTOWNICZYCH

The work is devoted to the study of shear strength of soldered joints fabricated by use of high-temperature solders of types Bi-11Ag, Au-20Sn, Sn-5Sb, Zn-4Al, Pb-5Sn, and Pb-10Sn. The shear strength was determined on metallic substrates made of Cu, Ni, and Ag. The strength of joints fabricated by use of flux and that of joints fabricated by use of ultrasonic activation without flux was compared. The obtained results have shown that in case of soldering by use of ultrasound (UT), higher shear strength of soldered joints was achieved with most solders. The highest shear strength by use of UT was achieved with an Au-20Sn joint fabricated on copper, namely up to 195 MPa. The lowest average values were achieved with Pb-based solders (Pb-5Sn and Pb-10Sn). The shear strength values of these solders used on Cu substrate varied from 24 to 27 MPa. DSC analysis was performed to determine the melting interval of lead-free solders.
*Keywords*: high-temperature solders, lead-free solders, shear strength, ultrasonic soldering, DSC analysis

Praca poświęcona jest badaniu wytrzymałości na ścinanie połączeń lutowanych wytwarzanych przy użyciu wysokotemperaturowych stopów lutowniczych typu Bi-11Ag, Au-20Sn, Sn-5Sb, Zn-4Al, Pb-5Sn i Pb-10Sn, na podłożach wykonanych z Cu, Ni i Ag. Porównano wytrzymałość spoin wytwarzanych przy użyciu topnika i spoin wytwarzanych przy użyciu aktywacji ultradźwiękowej bez topnika. Uzyskane wyniki wykazały, że w przypadku lutowania z wykorzystaniem ultradźwięków (UT), wyższa wytrzymałość na ścinanie połączeń lutowanych została osiągnięta dla większości stopów lutowniczych. Najwyższą wytrzymałość na ścinanie przy użyciu UT (tj. 195 MPa) uzyskano dla Au-20Sn na Cu. Najniższe średnie wartości zostały osiągnięte dla lutów na bazie Pb (Pb-5Sn i Pb-10Sn). Wartości wytrzymałości na ścinanie tych lutów na podłożach Cu waha się od 24 do 27 MPa. Analizę DSC przeprowadzono w celu określenia przedziału temperatur topnienia bezołowiowych stopów lutowniczych.

## 1. Introduction

The presented work is devoted to comparison of shear strength of the selected solders, which can be classed as the group of high-temperature solders. In spite of achievements obtained in the study of lead-free solders, there is still a need for the study of solders suitable for higher temperature applications. The type Pb-5Sn and Pb-10Sn solders are typical representatives of this group of solders with a high Pb content. Following the publications of Suganuma et al. [1] and Kim et al. [2] the solders based on Bi-Ag, Au-Sn, Sn-Sb, and Zn-Al alloys were selected as the basic ones for high-temperature lead-free solders.

Bi-11Ag solder, which exhibits acceptable melting point and price, also seems to be promising. However, several studies report its worse wettability on copper. Lalena et al. [3] studied the effect of a small amount of Ge on the wetting and mechanical properties of Bi-11Ag solder. Fima et al. [4] investigated the effect of alloying with Sn and Zn on wetting of Bi-Ag solder. Rottenmayr et al. [5] described, besides other aspects, the wettability of Bi-Ag solder containing from 2.6 to 12 wt. % Ag. The eutectic solder type Au-20Sn is suitable from the viewpoint of melting temperature, good electric and thermal conductivity, and also good wettability [6]. Unfortunately, its price seems to be an obvious disadvantage.

The Sn-5Sb based solders are typical, with good soldering properties and acceptable price. However, their relatively low melting point may be considered their disadvantage. El-Daly et al. [7] studied the effect of a third alloying element, namely Ag and Cu, on the thermal and mechanical properties of Sn-5Sb solder. The results showed that the melting point increased with the concentration increase of third element.

The solder type Zn-4Al was considered owing to its low price and good mechanical properties. Wettability and corrosion properties of this solder are still the subject of various studies. Osório et al. [8] investigated the corrosion properties of that solder and Takaku et al. [9] studied the interaction of Zn-4Al solder with the copper substrate.

Many previous studies have been devoted to the study of shear strength of high-temperature solders on Cu substrate. Works by Song et al. [10] were oriented to determination of shear strength in case of flux application. The other study of

* SLOVAK UNIVERSITY OF TECHNOLOGY IN BRATISLAVA, FACULTY OF MATERIALS SCIENCE AND TECHNOLOGY IN TRNAVA, INSTITUTE OF PRODUCTION TECHNOLOGIES, PAULÍNSKA 16, 917 24 TRNAVA, SLOVAK REPUBLIC

Shi et al. [11] analyses the effect of a small addition of rare earth metals on the shear strength of soldered joints.

Ultrasonic soldering meets the requirements concerning the speed and quality of joint fabrication. The corrosion resistance of soldered joints fabricated with ultrasound (UT) results mainly from the fact that no flux is necessary in this soldering technology. Lanin [12] described a method of UT soldering with the new solders with the aim to obtain longer joint life. The publication Koleňák et al. [13, 14] performed the comparison of shear strength of joints fabricated by use of UT and those soldered in vacuum. Ultrasonic-assisted soldering of Al was studied by Nagaoka et al. [15, 16]. In that case, the Zn-Al solder was used for soldering. The tensile strength of soldered joints was determined.

In this work, we performed the comparison of shear strength of joint soldered with the use of flux in the air and after UT soldering without flux. Cu, Ni, and Ag materials, which are mostly soldered in electronics, were applied as the substrates. Since experimentally fabricated solders were used for soldering, it was determined also the liquidus and solidus temperatures of the solders by DSC analysis. Based on the results of DSC investigations, the soldering temperature for fabrication of experimental specimens was proposed.

## 2. Experimental

Solders of the following composition were used in the experiments: Bi-11Ag, Au-20Sn, Sn-5Sb, Zn-4Al, Pb-5Sn, and Pb-10Sn. The melting interval of experimental solders was determined by DSC analysis. The equipment type NETZSCH STA 409 C/CD with processing software NETZSCH Proteus was employed. The analyses were performed in Ar protective gas with 99.999% purity. The heating rate of specimens with the average weight of 6 mg was 10 K/min. To accurately determine the solidus temperature, the Bi-11Ag solder was also analysed at a heating rate of 1 K/min. Pure tin with 5N purity was used for calibration and comparison purposes. The test specimens were made of substrates in the form of rings Ø 15 mm in diameter and 1.5 mm in thickness. Metallic substrates of Cu, Ni, and Ag with 4N purity were used. The test specimen is shown in Fig. 1-a.

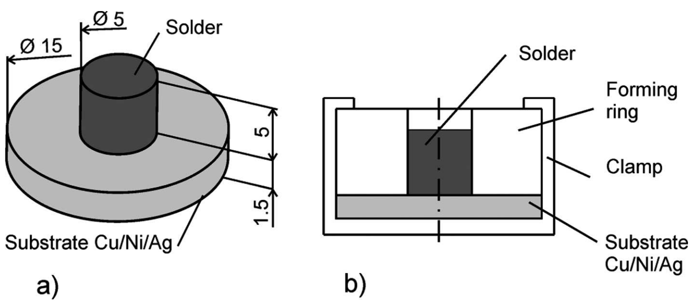


Fig. 1. Test specimen a) shape and dimensions, b) preparation procedure

The procedure for preparing specimens for the shear strength test was as follows (Fig. 1-b). A forming ring serving as a mould for the liquid solder is laid free on the parent metal. The forming ring must be coaxially oriented with the metallic substrate centre. Their mutual position is secured by sliding a clamp which simultaneously ensures a correct setting of the forming ring on the substrate due to a moderate pre-stressing.

Two variants of soldering with flux and without flux were used in specimen preparation:

1. Soldered joints were fabricated in the air with the use of $ZnCl_2$-$NH_4Cl$ based flux. The soldering temperature was 20°C higher than the liquidus of the tested solder. The dwell time of joints at soldering temperature was 60 seconds.
2. Soldered joints were fabricated in the air with UT application. The soldering temperature was 20°C higher than the liquidus of the tested solder. The dwell time at the soldering temperature was 30 seconds and the duration of the action of UT on the soldered joint was 5 seconds.

In both methods, specimen heating was provided by the hot plate with temperature control realized by use of a NiCr/NiSi thermocouple. UT equipment with 40 kHz frequency and 400 W output power with 2 $\mu$m amplitude was used for UT generation during soldering. The scheme and description of this equipment are shown in Fig. 2.

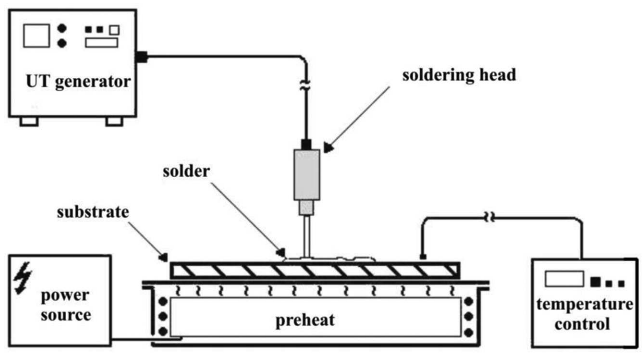


Fig. 2. Scheme of equipment for ultrasonic soldering

The shear strength was measured on equipment type LabTest 5.250SP1-VM at room temperature. A specially developed shearing jig was used for the directional change of the acting axial force. This jig provides a uniform specimen loading by shear in the boundary plane of the solder and substrate (see Fig. 3). The shear gap was selected as 0.1 mm, which corresponds to 2% of the sheared diameter of the pin formed of solder. The steady test rate was 0.5 mm/min.

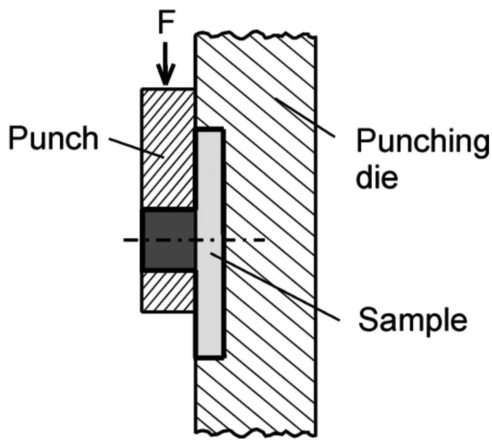


Fig. 3. Principal scheme of shear test

## 3. Results and Discussion

### 3.1. DSC analysis of high-temperature lead-free solders

DSC analysis was performed in order to identify the melting points of type Bi-11Ag, Au-20Sn, Sn-5Sb, and Zn-4Al lead-free solders. The description of the results of DSC analysis was complemented by the results of EDX analysis. In Figure 4 the DSC curve of Bi-11Ag solder is shown. It is visual that the Bi-11Ag solder shows a wide melting interval. At a temperature of 263.1°C the solder matrix formed of fine eutectics (Bi + 3-4 wt. % Ag) started melting and at a temperature of 266.8°C the solder matrix was fully molten. The silver phases segregated in the solder matrix were fully molten at 371.2°C so, the Bi-11Ag solder was completely molten above this temperature. The Au-20Sn type gold based solder was of eutectic composition and it starts melting at a temperature of 280.2°C (see Fig. 5). The Sn-5Sb solder is characterized by its peritectic reaction and according to the DSC curve (Fig. 6), it starts to melt at a temperature of 240.3°C and the melting process was fully completed at 243.9°C.

TABLE 1

The results of DSC measurement

| Solder | Bi-11Ag | Au-20Sn | Sn-5Sb | Zn-4Al |
|---|---|---|---|---|
| Heating | 10 K/min | 10 K/min | 10 K/min | 10 K/min |
| Temperature range of measurement [°C] | 60 to 500 | 22 to 450 | 200 to 280 | 45 to 500 |
| Onset temperature [°C] | 263.1 | 280.2 | 240.3 | 380.7 |
| Peak temperature [°C] | 266.8 | 294.5 | 242.9 | 386.5 |
| End temperature [°C] | 371.2 | 302.8 | 243.9 | 411.5 |

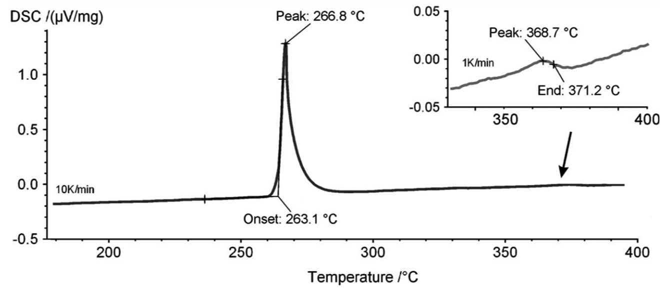


Fig. 4. DSC curve of Bi-11Ag solder

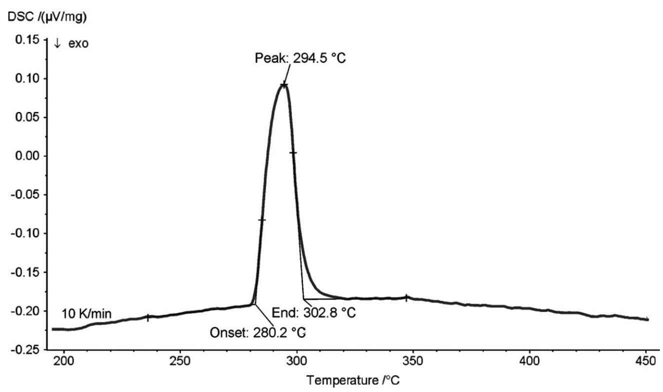


Fig. 5. DSC curve of Au-20Sn solder

The last studied solder, type Zn-4Al, showed a wide melting interval. At a temperature of 277.6°C the start of eutectoid transformation was observed (Fig. 7). According to the publication of Takaku et al. [9] the following reaction: Al-rich fcc + hcp (Zn) / Zn-rich fcc, takes place at the same temperature. The eutectics (Zn + 6 wt.% Al) segregated on the grain boundary of the solder zinc matrix start to melt at a temperature of 380.7°C and the melting temperature of (Zn) solid solution was determined at 411.5°C.

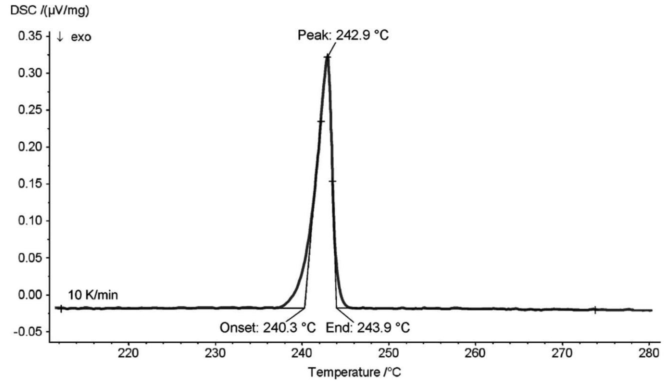


Fig. 6. DSC curve of Sn-5Sb solder

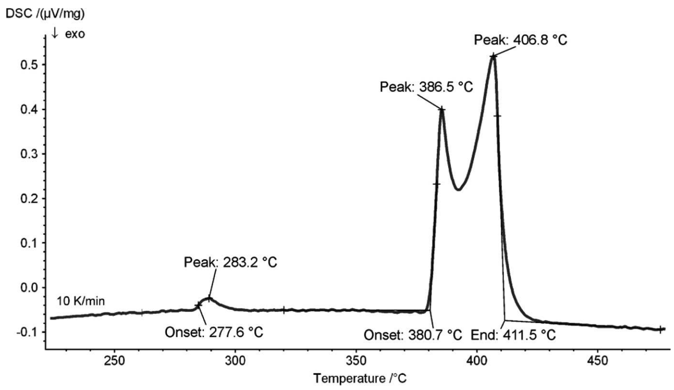


Fig. 7. DSC curve of Zn-4Al solder

### 3.2. Measuring the shear strength of joints

Based on the data obtained from the DSC analysis, test pieces for the shear strength study were prepared separately. The average values from six measurements of shear strength are documented in Figs. 8 and 9. It was found that the shear strength values of joints fabricated by ultrasonic soldering are higher than in case of soldering with flux. The highest shear strength, equal to 195 MPa, was measured for the Au-20Sn joint fabricated on copper by the use of UTand the lowest one for Pb based solders (Pb-5Sn and Pb-10Sn). Their average values of shear strength on Cu substrate varied from 24 to 27 MPa. The low tin content in these solders causes the formation of a relatively narrow zone of transient intermetallic compounds that mostly strengthen the transition zone, where shear strength is determined.

Our measurement results of the shear strength obtained for the copper – solder (Bi-11Ag and Pb-5Sn) joints are comparable with the results of Shi et al. [11]. The average value of shear strength obtained in that work with Bi-10Ag solder varied from 22 to 42 MPa and in case of Pb-5Sn solder from 18 to 30 MPa. In both cases soldering was performed by the use of $ZnCl_2$-$NH_4Cl$ flux. In the work of Song et al. [10] the lap joint was used to determine the shear strength of joint fabricated by the use of Bi-11Ag solder on copper and obtained results showed the values from 20 to 36 MPa and for the Pb-5Sn solder the shear strength between 14 and 18 MPa was measured.

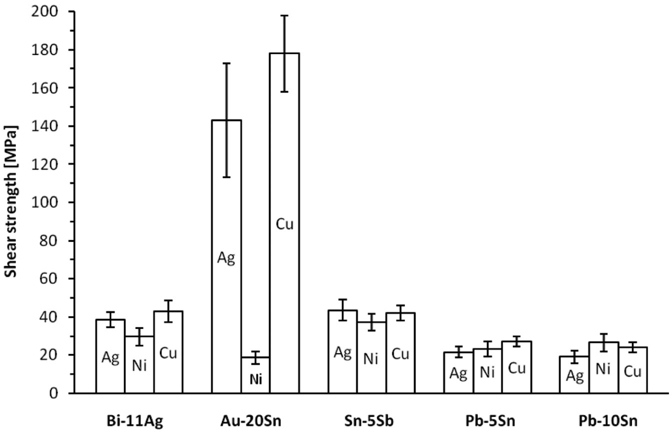


Fig. 8. Shear strength of joints fabricated by use of $ZnCl_2$-$NH_4Cl$ flux

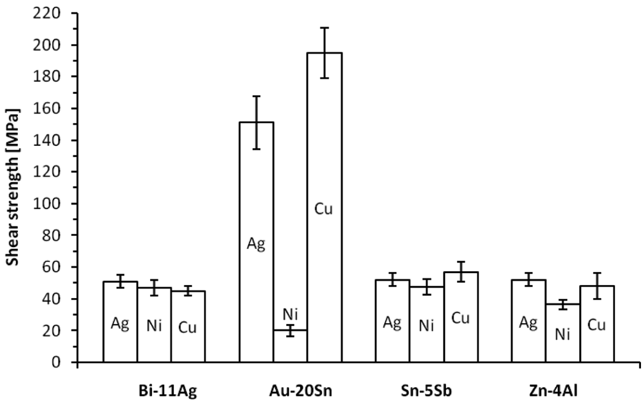


Fig. 9. Shear strength of joints fabricated without flux by use of 40 kHz ultrasound

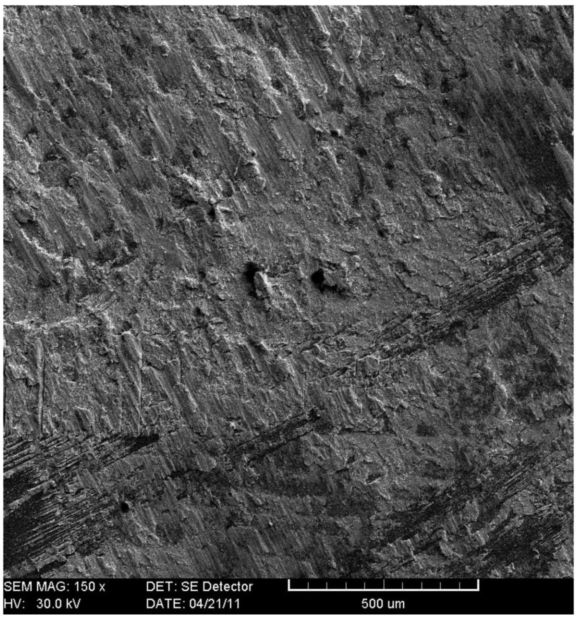


Fig. 10. Fractured surface of Bi-11Ag solder on Cu substrate

Fractographic analysis was applied in the study of fracture morphology by use of SEM observations. It was investigated using specimens with Cu substrate fabricated by the UT soldering. The ductile fracture was observed in all cases. In Figure 10 the fractured surface of Bi-11Ag solder is showed. In case of Bi-11Ag solder, the fracture occurred on the intermetallic boundary. Coarsening of Cu substrate is elucidated by the capability of Bi-11Ag solder to roughen the surface and to penetrate to the grain boundaries [17, 10]. In case of Au-20Sn solder, tearing out of a part of the Cu substrate also occurred (Fig. 11) and the fracture formed partially in the solder and partially in the Cu substrate. The micrographs of ductile fracture of a joint in Sn-5Sb solder is shown in Fig. 12 and in Fig. 13 a similar fracture in Zn-4Al solder is visual, too. In both joints fracture occurred just in the solder.

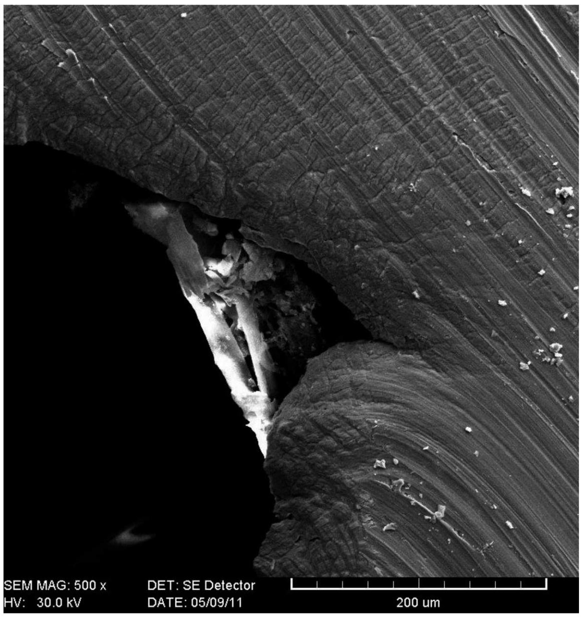


Fig. 11. Fractured surface of Au-20Sn solder with a partial tearing out of Cu substrate

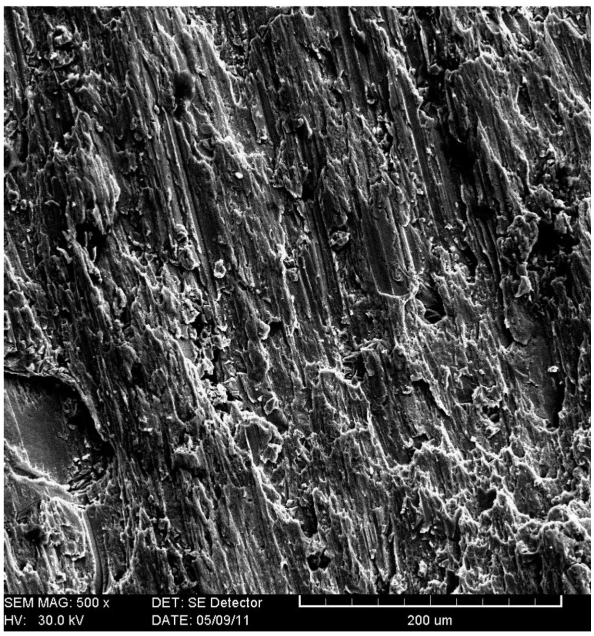


Fig. 12. Detail of ductile fracture of Sn-5Sb solder

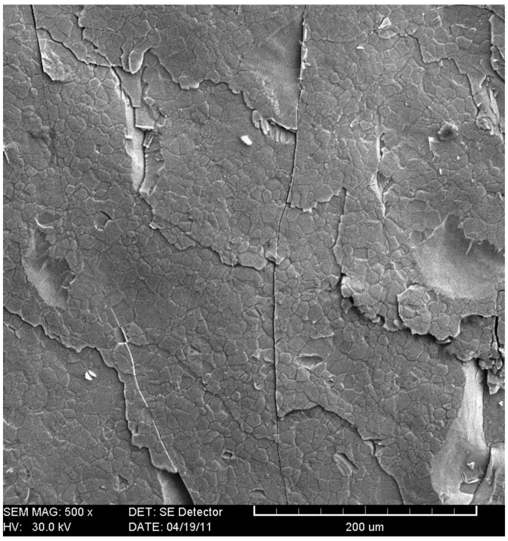


Fig. 13. A view on damaged zone of Zn-4Al solder and Cu substrate

## 4. Conclusions

High-temperature solders of the composition Bi-11Ag, Au-20Sn, Sn-5Sb, Zn-4Al wetted the Cu, Ni and Ag substrates without flux, when the ultrasonic activation was applied. The observed wetting angles $\alpha$ changed between $0° < \alpha < 20°$.

It was found that classical lead containing solders, as Pb-5Sn and Pb-10Sn, did not wet the Cu, Ni and Ag substrates by the ultrasonic activation. Wetting of these substrates was observed when the $ZnCl_2$-$NH_4Cl$ flux was applied.

Joints obtained by the UT soldering were characterized by higher shear strength in comparison to these which were prepared by soldering with flux because owing to cavitation caused by UT power, the interaction of solder with the substrate was improved. Also the wetting angle was reduced resulting in the higher shear strength of soldered joints.

The highest shear strength (195 MPa) was achieved for the Cu/Au-20Sn joint and the lowest one (19 MPa) was observed for the Ni/Au-20Sn joint.

The fractographic analysis has revealed that fracture in Cu/Bi-11Ag joint occurred on intermetallic boundary. In case of Au-20Sn solder, the fracture occurred with a partial tearing off of the Cu substrate and in case of Sn-5Sb and Zn-4Al solders, the fracture occurred exclusively in the solder.

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