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Research article

Investigation of microstructure and wettability of selected lead-free solders for higher application temperatures

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Abstract: The work deals with the investigation of thermal properties and wettability of lead-free solders for higher application temperatures. For the research, the experimental solders SnSb5, ZnAl4, ZnAl6Ag6 and BiAg11 were used. For investigation of wettability, Ag, Cu and Ni substrates was used. To measure the solders melting intervals and their thermal properties, the DSC analysis was realized. The measurement of wettability was carried out in a controlled atmosphere by trigonometric method. Zn based solders wets none of the examined substrates. SnSb5 solder wets only Cu substrate with wetting angle of 54°. Soldering alloy BiAg11 wets all substrates, wherein the best result (23°) was achieved on Ag substrate. Shear strength of BiAg11 and SnSb5 joints reached higher value then classic PbSn5 solder.

Keywords: solder; substrate; thermal properties; wetting; protective atmosphere

1. Introduction

Traditional Sn–Pb solders were the solders most used for electronic equipment in the past. However, since lead is a toxic substance detrimental to human health, manufacturers were forced to use other alternatives for soldering materials.

Solders for high-application temperatures are often used for connecting the components of casings for power semiconductors. Such power electronics is employed in the automotive, space, aviation and power generation industries. These are mainly applications like the electronics of motor control, exhaust and brake systems, parts for electric and hybrid cars, as well as circuit boards etc. [1–4].

The alternative alloys to replace solders with high lead content are investigated in this paper. In the case of high-application temperatures, the main alternatives for solders are based on Sn–Sb, Bi–Ag and Zn–Al or Zn–Sn [5–8]. The research is oriented toward Zn–Al based solders with the addition of other elements for lowering melting point and improving their technological properties during soldering. Mainly the Zn–Al–Mg–Ga, Zn–Al and Zn–Cu–Al solder types are considered [9–12].

Solder type Bi–Ag represents another alternative. The melting point of these solders varies within a range from 250 to 400 °C. Their lower electric conductivity may be considered a drawback compared with high-lead solders. The following studies were devoted to microstructure, wettability and shear strength of of Cu/Cu fabricated soldered joints with Bi–Ag based solders [7,13–15]. The results proved that the soldered joints of Bi–Ag/Cu attain higher shear strength values when compared to Pb–Sn/Cu joints.

The Sn–Sb solder with lower Sb content than 5 wt% exerts excellent mechanical properties without the formation of IMC. Research upon the properties of these solders was performed by the authors [3,16]. Other solders destined for high-application temperatures may include the type Sn–Ag–Sb solders. The authors [17,18] studied the effect of Sb proportion in the solder upon the reliability of joints fabricated with copper. They found that with increasing Sb content, the life of joints and solder wettability were also improved.

This research solves the selected characteristics of solders destined for high-application temperatures, thus dealing with solders type Sn–Sb, Zn–Al, Zn–Al–Ag and Bi–Ag. The following criteria were selected in the study of properties of solder alloys for high-application temperatures: initial condition of the microstructure, melting interval of solder within 260 °C to 420 °C and wettability, mainly on silver, nickel and copper substrates with a minimum shear strength of 15 MPa.

These alloys may serve as suitable alternatives to solders with Pb content. The thermal transformations and intervals of melting point of these solders were determined by use of DSC analysis. The main criterion of solderability consists in wettability of solders on different substrates. For this reason, the wettability on the substrates used in electronics was studied, such as Cu, Ni and Ag. The research is also aimed toward the measurement of shear strength attained on the substrates mentioned.

2. Materials and methods

To measure the solders melting intervals and their thermal properties, DSC (Differential Scanning Calorimetry) analysis was used. Solder alloys were assessed experimentally, produced by melting in a vacuum and thus the melting interval was unknown. Experiments were carried out by a NETZSCH STA 409 C/CD device.

Solder samples of approximately 6 mg were placed in an aluminum pan of Al_2O_3 ceramic and covered with a cap. Temperature range measurements were selected considering the expected interval of solder melting and anticipated temperatures of phase transformations. DSC analysis was performed to identify the melting point of the Sn5Sb, Zn4Al, Zn6Al6Ag and Bi11Ag lead-free solders.

Measurements of wettability by trigonometric methods were carried out with Sn5Sb, Zn4Al, Zn6Al6Ag and Bi11Ag solders in a protective atmosphere (90% N_2 + 10% H_2). The wetting measuring device is shown in Figure 1. A portion of the hydrogen in the protective atmosphere serves the effect of reducing metal oxides. To compare the wettability in BiAg11 solder, $ZnCl_2$–NH_4Cl activated flux was used. A contact angle on the contact surface of Cu, Ni and Ag substrates with dimensions of Ø 15 × 1.5 to 2.5 mm was detected. To the middle of substrates made of the base material, a cubic solder sample with an edge length of 4 mm was deposited. The scheme of the sample is shown in Figure 2.

The microstructure of those soldered joints analyzed was studied with scanning electron microscopy (SEM) on Tescan Vega TS 5130 MM and JEOL 7600 F microscopes. The quantitative and semi-quantitative chemical microanalysis of solder was performed on a JEOL 7600 F microscope with X-ray Microspec WDX-3PC microanalyzer.

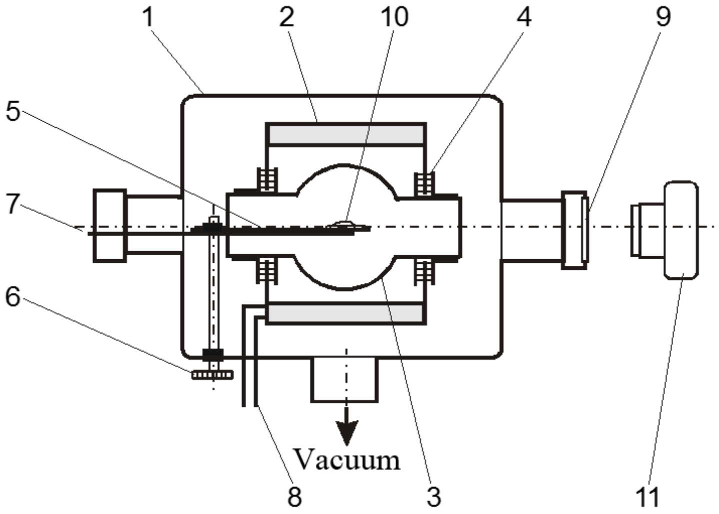


Figure 1. Schematic representation of apparatus for wettability measurement. 1: vacuum bell, 2: cooling body of the oven, 3: graphite oven, 4: fastening ceramic pins, 5: feeder, 6: feeder controller, 7: thermocouple, 8: inlet and outlet of cooling water, 9: observation hole for photography, 10: specimen, 11: photo camera.

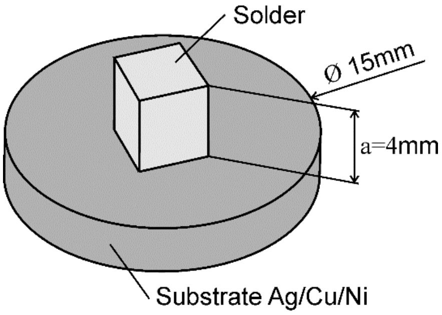


Figure 2. Scheme of the sample.

Shear strength testing was done to determine the mechanical properties of the soldered joints. Measurements were taken on Ag/Ag, Ni/Ni and Cu/Cu joints. The specimens were prepared in the Ø 15 × 3 mm and 10 × 10 × 1.5 mm dimension, according to special jig construction.

Shear strength was determined by LabTest 5.250SP1-VM versatile tearing equipment. The shear jig ensured a uniform loading of the test specimen by shear in the plane of solder and substrate interface. The specimen for measurement of shear strength is documented in Figure 3.

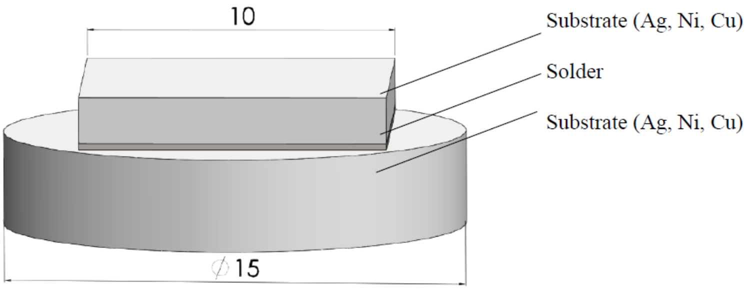
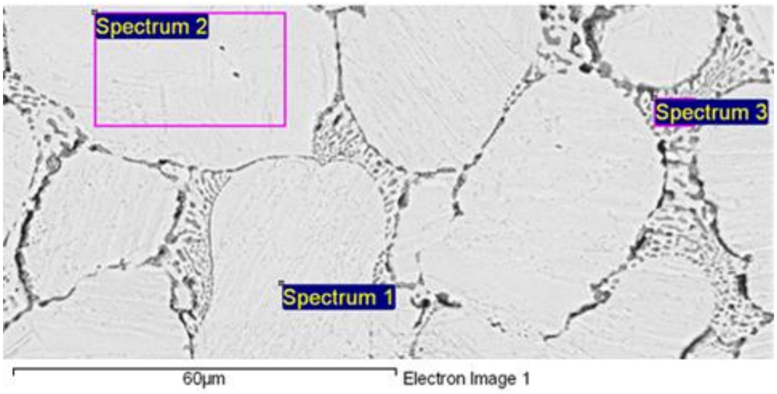


Figure 3. The specimen for measurement of shear strength.

3. Results

3.1. Microstructure analysis

The quantitative analysis of Zn4Al solder is given below Figure 4. Two solid solutions (Zn) and (Al) with a limited solubility occur in the binary Al–Zn system. Owing to limited solubility, the eutecticum and eutectoid mixture of these solid solutions occur in the system. The matrix of Zn4Al solder (Figure 4) is composed of great grains of the solid solution (Zn) with concentration of 98.68 wt% Zn. A fine eutecticum, formed of solid solutions (Zn) + (Al) is segregated along the grain boundaries.



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

Figure 4. Microstructure of Zn4Al solder.

The microstructure and BSE analysis of Bi11Ag solder is shown in Figure 5. Analysis was carried out in three areas of the structure: base matrix, inside the particles embedded in a matrix and in the immediate vicinity of the particles. Dark particles are mostly excluded crystals of approximate composition (95% Ag + 5% Bi). The immediate vicinity of the particles is almost pure bismuth (Ag content is in the range of 0.1–0.2%). The base matrix is a very fine eutectic containing about 3 to 4% of Ag, the remainder being Bi.

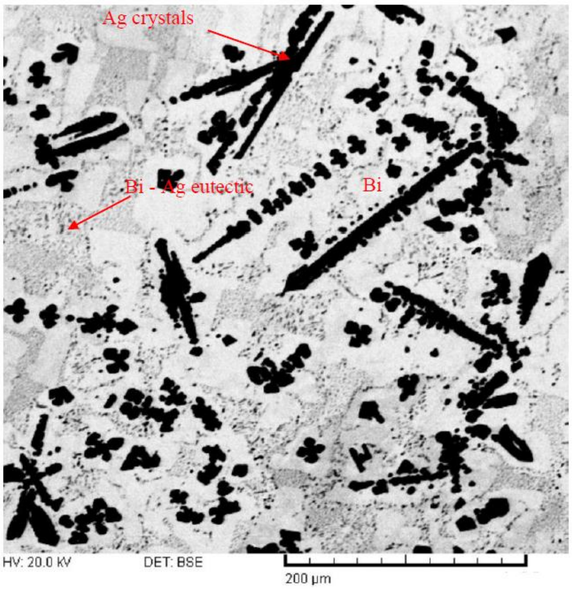


Figure 5. BSE analysis of Bi11Ag solder.

Figure 6 shows the microstructure of Zn6Al6Ag solder. The brightest particles are characterized by an intermetallic compound of $AgZn_3$. Less bright areas are composed of a solid solution of (Zn). The dark areas exhibit a eutectic mixture formed of a solid solution of (Zn) along with solid solution of (Al). The most darker areas exhibit a solid solution of (Al ´). The solder is not composed with a pure Ag.

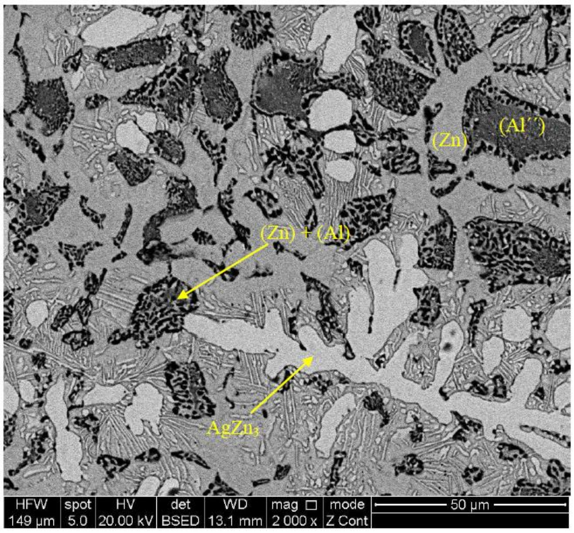


Figure 6. Microstructure of Zn6Al6Ag solder.

This chapter was devoted to the assessment of solders from the viewpoint of their microstructure. The Zn4Al solder is of next-to-eutectic composition. The pure eutectics is attained at the Al content of 6 wt%. Solder structure is thus formed of a eutectic and eutectoid mixture of α and β solid solutions. Zinc and 6 wt% Al in the alloy create a eutectic composition. Silver in Zn6Al6Ag solder forms an intermediate $AgZn_3$ phase after its peritectic reaction. The Sn5Sb solder structure is also after peritectic reaction.

The solder with Bi11Ag composition has a broader melting interval, though the Bi–Ag system is of a simple eutectic type and the solder structure is formed of a eutectic mixture of a solid solution of (Bi) and (Ag). The BiAg solder was of pure eutectic composition at the Ag content of 3 wt%, which means that the solder ought to be designated as Bi3Ag. Regarding their microstructure, the most suitable solders for high-application temperatures are types Zn4Al, Zn6Al6Ag and Bi11Ag, since these exert near-to-eutectic structure.

3.2. DSC analysis

The main objective of DSC analysis was to determine the melting interval of each solder alloy. The result of measurement is a DSC curve, which is a plot of heat flow. The Sn5Sb solder is characterized by its peritectic reaction. According to the DSC curve (Figure 7), the solder begins to melt at 240.3 ℃. Melting is complete at 243.9 ℃.

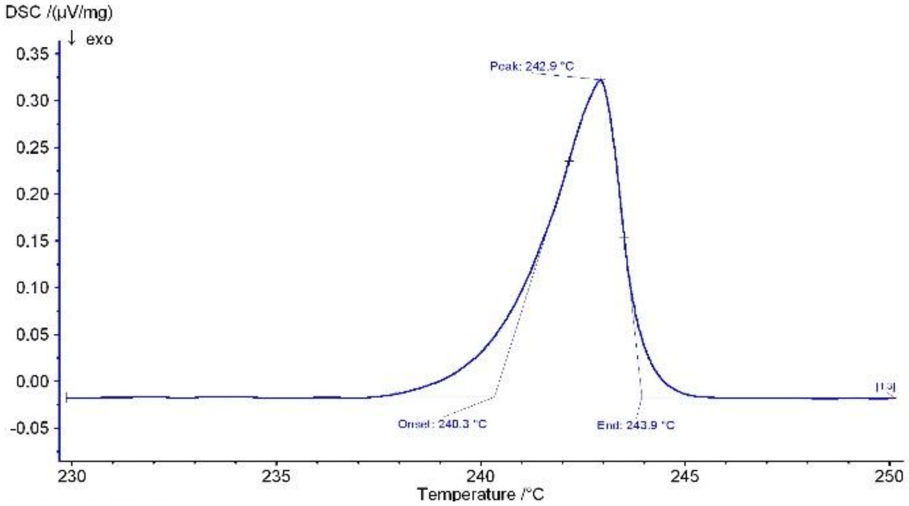


Figure 7. DSC analysis of Sn5Sb.

The next solder investigated, Zn4Al, has a wide melting interval. 277.6 ℃ marks the beginning of eutectoid transformation (Figure 8). At this temperature, the reaction of Al rich fcc + hcp (Zn)/Zn-rich fcc occurs. At a temperature of 380.7 ℃, eutectic Zn + 6 wt% Al, excluded to the grain boundaries of zinc solder, begins to melt. Solid solution (Zn) achieved a completely liquid state at a temperature of 411.5 ℃.

Zn–Al based solder with the addition of 6 wt% of Ag was a further investigated solder. 287.4 ℃ marks the beginning of eutectoid transformation (Figure 9) as is the case of Zn4Al solder. The solder begins to melt at 390.9 ℃ and melting is complete at 399.2 ℃.

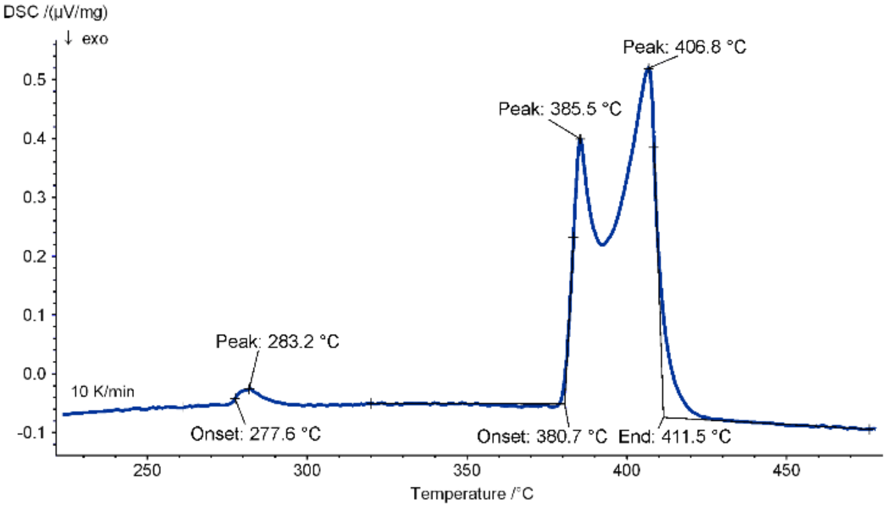


Figure 8. DSC analysis of Zn4Al solder.

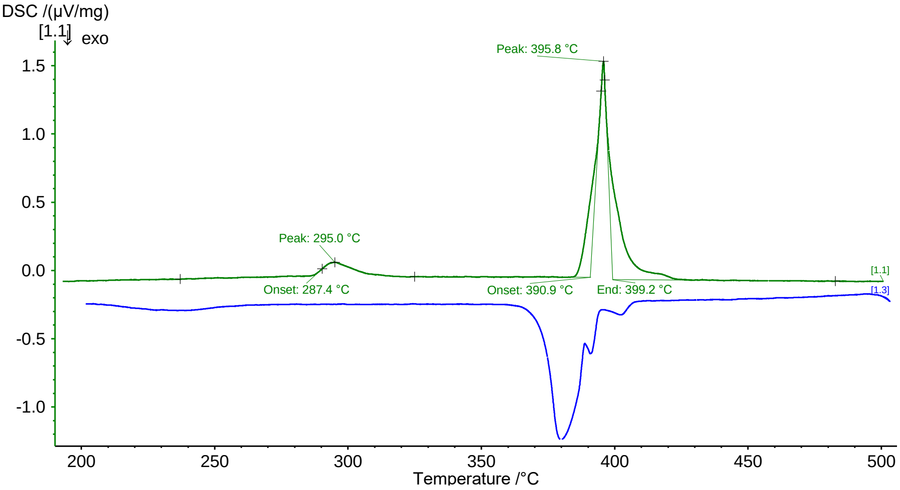


Figure 9. DSC analysis of Zn6Al6Ag solder.

Bi11Ag solder (Figure 10) has a wide melting interval. At 263.1 °C, the matrix of solder created from the fine eutectic (Bi + 3 to 4 wt% of Ag) begins to melt. At 266.8 °C, the matrix is molten. Silver crystals excluded in the matrix of solder are completely melted at 371.2 °C. Above this temperature, the Bi11Ag experimental solder is completely melted.

From the results of DSC analysis, the following findings were indicated on the basis of melting temperatures of solder: the tin-based solder type Sn5Sb is typical, with a relatively low melting point, which is a drawback in the case of high-temperature applications. However, a narrow interval is rather to its advantage. The melting interval varies between 240 to 244 °C.

Zn-based solders (Zn4Al and Zn6Al6Ag) are oppositely typical, with high melting temperatures, even above 380 °C. Their advantage consists in a rather broad melting interval. In the case of Zn4Al solder it varies from 380.7 to 411.5 °C and for Zn6Al6Ag solder it varies from 390.9 to 399.2 °C.

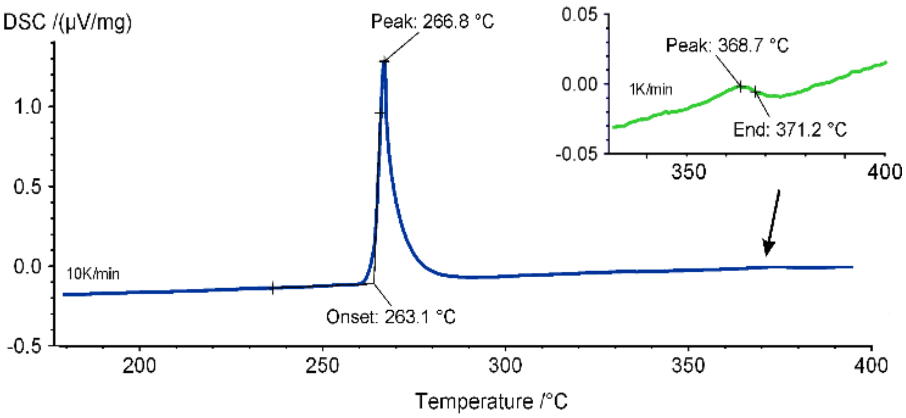


Figure 10. DSC analysis of Bi11Ag solder.

The Bi-based (Bi11Ag) solder is more typical with an appropriate melting point, but its drawback consists of a rather broad melting interval, varying from 263 to 371 ℃. The mentioned results are valid, if we consider an optimum melting interval to be the range from 302 to 314 ℃, which corresponds to the melting temperatures of classical Pb5Sn and Pb10Sn solders.

Regarding the results of DSC analysis, Bi11Ag solder may be considered an acceptable substitute.

3.3. Wettability of examined solders

The wettability of Sn5Sb solder was evaluated on a base material of Ag, Cu and Ni. The results are documented in Figure 11 and show that Sn5Sb solder at 260 ℃ only wets Ag and Ni substrate with a large wetting angle of about 90 °, even on a long hold at soldering temperature (30 min). Better results of wettability were achieved on the copper, which at 30 min had a contact angle of 54 °.

The wettability of Zn4Al solder was equally evaluated on a base material of Ag, Cu and Ni. Figure 12 documents those measurement results. The wettability results, according to Figure 12, indicate that at soldering temperature 480 ℃ and a holding time of 30 min, Zn4Al solder fails to wet substrates of Ag, Cu and Ni when soldering in a protective atmosphere (90% N_2 + 10% H_2).

For the same substrates, Zn6Al6Ag solder was also used. The result of the experiments, as shown in Figure 13, indicate that the solder fails to wet the substrate.

The latest experimental solder alloy was Bi11Ag. Soldering temperature was 380 ℃. The measurement results of wettability in a protective atmosphere are documented in Figure 14. Best wettability of soldering in a protective atmosphere was reached in the Ag substrate. The contact angle at the time of 30 min reached 25 °. The worst wettability recorded was on the Cu substrate, where at 30 min, the contact angle reached 55 °.

For comparative purposes, identical measurement techniques for the measuring of wetting angles of Bi11Ag solder (Figure 15) were undertaken, using $ZnCl_2$–NH_4Cl flux. Cu and Ni alloy wets the substrate only with a large wetting angle. A satisfactory wettability of 21 ° was observed on the Ag substrate.

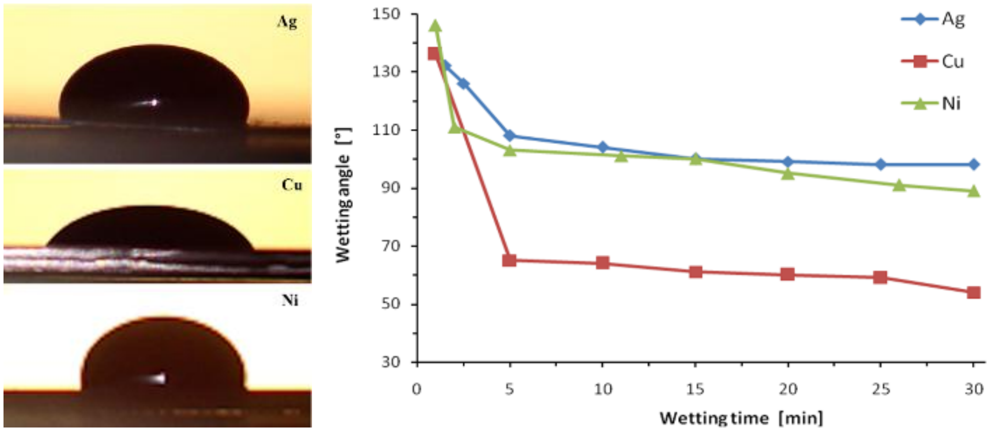


Figure 11. Wettability of Sn5Sb solder at the soldering temperature of 260 °C.

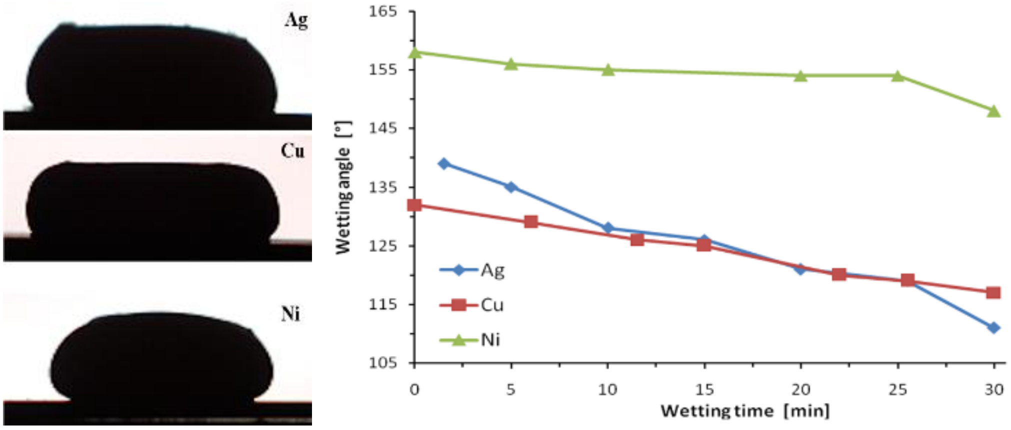


Figure 12. Wettability of Zn4Al solder at soldering temperature of 480 °C.

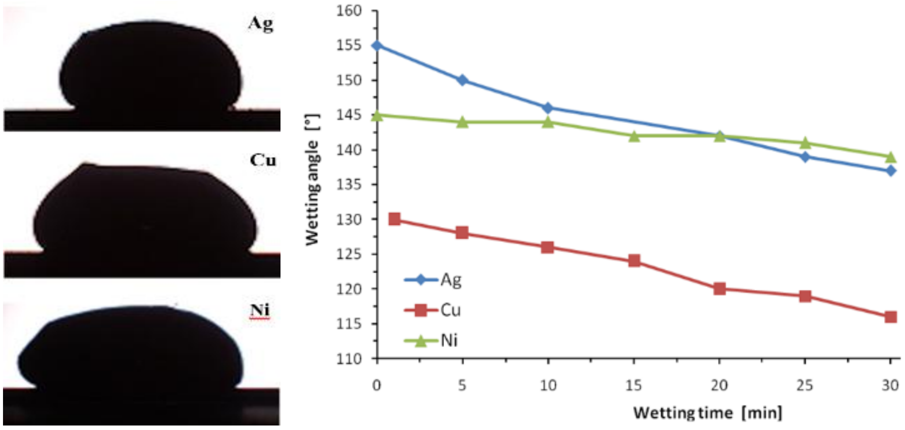


Figure 13. Wettability of Zn6Al6Ag solder at soldering temperature of 480 °C.

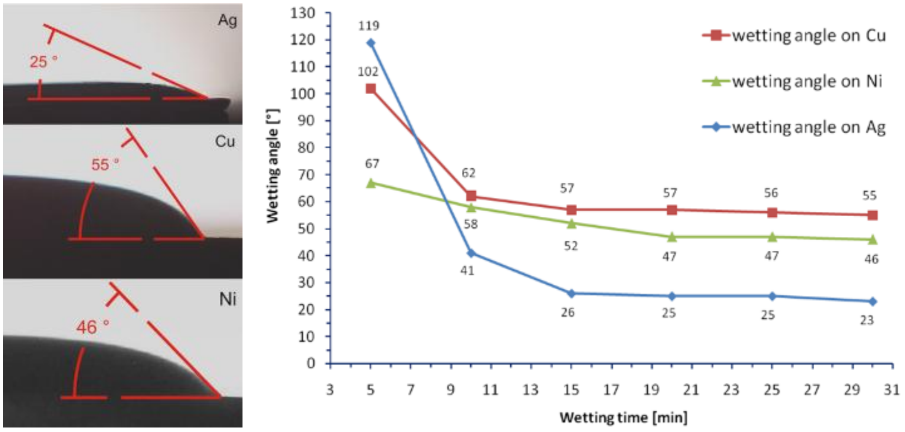


Figure 14. Wettability of Bi11Ag solder at soldering temperature of 380 °C.

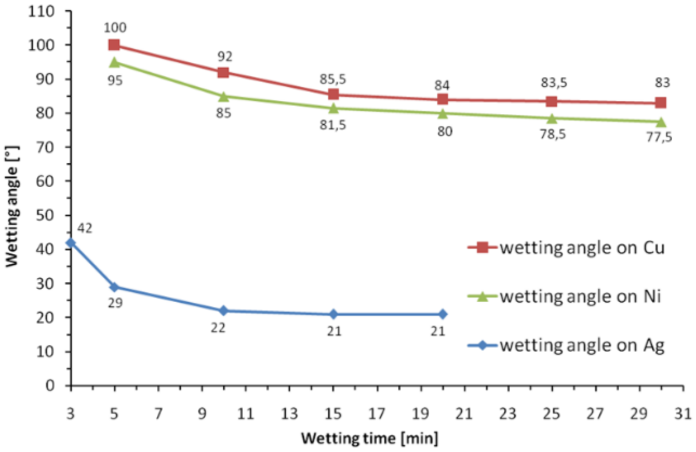


Figure 15. Wettability of Bi11Ag solder at soldering temperature of 308 °C using $ZnCl_2$–NH_4Cl flux.

Based on the results of wettability tests made on Ag, Cu and Ni substrates, Sn5Sb, Zn4Al, Zn6Al6Ag and Bi11Ag solders can be summarized as follows: The Zn-base solder (Zn4Al, Zn6Al6Ag) wetted none of the substrates studied. The tin-based Sn5Sb solder has wetted just the Cu substrate with a wetting angle of 54 °. The surface of Ag and Ni substrates was not wetted at all. The most suitable wettability was shown by Bi-based Bi11Ag type solder, which wetted all substrates studied. Its wetting angle on silver surface was 23 °, on nickel 46 ° and on the copper surface it registered 55 °.

These results apply to wettability tests performed under the protection of shielding gas (90% N_2 + 10% H_2) and supposed that as a wettability limit we consider the wetting angle of 90 °. Regarding its wettability properties, the Bi11Ag soldering alloy may be considered the most suitable solder.

3.4. Shear strength measurement

Shear strength measurements were performed on all solders studied. The shear strength of Pb5Sn, the recently most used solder type, also destined for higher application temperatures, was measured for comparative purposes. The Zn4Al and Zn6Al6Ag solders failed to wet any of Cu, Ni and Ag substrates upon application of $ZnCl_2$–NH_4Cl flux. Therefore a strength measurement of joints fabricated with these solders was not performed. The average values from six measurements of shear strength of joints fabricated with Bi11Ag, Sn5Sb and Pb5Sn solders are shown in Figure 16.

From the results of shear strengths of soldered joints, shown in Figure 16, it is obvious that the highest strength values were achieved with Sn5Sb solder, where the highest average shear strength of 42 MPa was attained on the copper substrate. These values of shear strengths are comparable with the Bi11Ag-based solders. The lowest shear strength values (20 to 26 MPa) were achieved by soldering with the classical lead Pb5Sn solder. Thus, it must be recognized that the Pb5Sn solders exert just roughly half the overall shear strength values when compared with Bi11Ag and Sn5Sb-based solders. Regarding the set criterion of shear strength of joints, the solders type Bi11Ag and Sn5Sb appear to be the most acceptable.

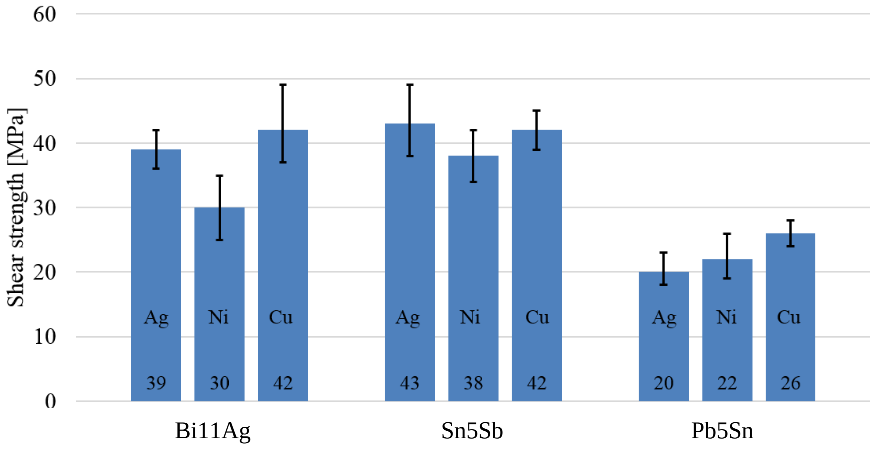


Figure 16. Shear strength measurement of solder joints.

4. Conclusions

The experiment dealt with the study of properties of the selected lead-free solders destined for high-application temperatures. On the basis of the set criteria of microstructural conditions, melting intervals of the solders, wettability and shear strength, the following results can be summarized:

- Regarding the microstructure of solder for high-application temperatures, the most suitable are the Zn4Al, Zn6Al6Ag and Bi11Ag solders, since these exert near-to-eutectic structure.
- Regarding the results of DSC analysis, the Bi11Ag solder may be considered an acceptable substitute. Though this solder exerts a rather broad melting interval, its melting point most approaches the melting interval of classical Pb5Sn and Pb10Sn solders. The tin-based Sn5Sb solder is typical, with a relatively low melting point, which is a drawback from the viewpoint of high-temperature applications. The Zn-based solders, Zn4Al and Zn6Al6Ag, are to the contrary, typical of those with high melting points above 380 °C.
- The most suitable wettability is shown by the Bi-based Bi11Ag solder, which wetted all substrates studied. The wetting angle on silver surface was 23°, on nickel 46° and 55° on the copper surface. The results mentioned are valid for wettability tests performed under the protection of a shielding atmosphere (90% N_2 + 10% H_2).

- Regarding the criterion of shear strength of joints, both Bi11Ag and Sn5Sb solders are acceptable. The Sn5Sb solder reaches the shear strength of 38 to 43 MPa and the shear strength of Bi11Ag solder varies from 39 to 42 MPa. These solders exert twice the shear strength of Pb–Sn solders.

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Conflict of interest

All authors declare no conflicts of interest in this paper.

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