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Review

# Soldering of aluminium with copper and steel using intermediate layer Zn–Ni

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A B S T R A C T

Nowadays, the possibility of bonding together materials significantly differing from each other with respect to physico-chemical and mechanical properties becomes more and more important. This is because of constantly increasing demand for modern facilities that are able to cope with increasing ecological and economical requirements in various industries, like power engineering, refrigerating engineering, heating or air-conditioning industries. This group of bondings includes soldered joints of aluminium with other metals, like copper, unalloyed steel and alloyed steel. However, bonding together these materials is related to numerous problems resulting from variable physico-chemical and mechanical properties of the metals to be bonded. There is also a risk that hard intermetallic phases will be created, entailing brittleness of soldered joints [4,5].

In the paper, presented is the way of limiting occurrence of intermetallic phases on the interface between aluminium and other metals by galvanic application on their surfaces a layer Zn–Ni. Presented are measurements of wettability and spreadability of zinc-based solders on substrates with the applied layer, as well as metallographic examinations, microhardness measurements and shear tests of soldered joints.

## 1. Introduction

Obtaining correctly made soldered joints, meeting the imposed operational requirements, is conditioned by occurrence of basic physico-chemical phenomena on the surface of base material [1–3,11]. First of all, ensured should be possibly best wettability and spreadability of the used solders, which in consequence facilitates occurrence of capillary phenomena and tight filling the soldering gap with liquid solder. Therefore, quality of a soldered joint is to a large degree dependent on proper selection of auxiliary materials for flame soldering, i.e. solders and fluxes. If it does not usually make a greater problem in the case of similar-metal joints, selection of

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suitable auxiliary materials for dissimilar-metal joints is much more complicated and often creates many problems. This is caused by absence of universal solders and fluxes well wetting surfaces of a wide group of materials. This is especially difficult in the case of making dissimilar-metal joints with aluminium that is one of harder solderable engineering materials, which is decided by its following properties [5–9]:

- low melting point of aluminium (ca. 660 °C) hindering selection of a solder,
- presence of high-melting (2050 °C) and chemically durable (11,163 kJ/mol $O_2$) layer of oxides $Al_2O_3$ hermetically covering surface of aluminium,
- low mechanical properties, especially at temperatures over 500 °C,
- high thermal conductivity (237 W/m K) and expansion ($26 \times 10^{-6}$ $K^{-1}$), as well as considerable volume contraction (7%), which are conducive to creation of thermal stresses and deformations.

The solders type Zn–Al, used for soldering, well wet surfaces of aluminium grade EN AW-1050A, low-alloyed steel grade DC01 and acid resistant steel grade X5CrNi18-10. However, they do not guarantee sufficient wettability of copper grade Cu-ETP [9]. Insufficient wettability of copper with zinc-based solders does not make the only problem. As announced in [9], on the interface between Zn-solders and copper Cu-ETP and steel DC01 created are hard reactive zones entailing brittleness of soldered joints with aluminium. The reactive zones can be composed of intermetallic phases of the system Al–Cu or Al–Fe [11–13]. Identification of these phases requires X-ray diffraction analysis.

A solution for elimination of hard zones in dissimilar-metal soldered joints with aluminium can be using a properly thick galvanic coating Zn–Ni that would play a part of a diffusion barrier. It was demonstrated in [9] that a 20 μm thick zinc layer applied on surface of unalloyed steel by hot galvanising effectively restricts forming a reactive zone on the interface between substrate and solder. However, in comparison with a Zn layer, the Zn–Ni layer demonstrates ten times higher corrosion resistance (as proved by tests in a salt spray chamber). It should also ensure improvement of wettability of Cu-ETP copper by zinc-based solders.

## 2. Materials used in the research

Dissimilar-metal soldered joints with aluminium were made using a Zn–Al solder with Al content not exceeding 15 wt% [4,6,7,9]. Chemical composition, melting point and form of the applied Zn–Al solders are presented in Table 1. Used was also a non-corrosive flux 192 NX made by Castolin in form of paste, containing compounds of caesium. The flux activity temperature ranges between 420 and 470 °C [10].

The base material used in the soldering tests was aluminium AW-1050A acc. to EN 573-3:2010 with chemical composition given in Table 2.

To make dissimilar-metal soldered joints with aluminium, chosen was copper Cu-ETP and unalloyed steel DC01, whose chemical compositions are given in Table 3. These metals were selected with respect to occurrence of reactive zones on interface with zinc-based solders [9].

## 3. Galvanic application of Zn–Ni layer on surfaces of copper and unalloyed steel

The main task of the Zn–Ni layer was elimination, by creating a diffusive barrier, of brittle intermetallic phases that are formed on the interface of dissimilar-metal soldered joints with aluminium, made with zinc-based solders. The applied Zn–Ni layer should be also characterised by good soldering properties, i.e. guarantee good wettability and spreadability of solders used in the examinations.

Before applying the Zn–Ni coating, it was necessary to prepare suitably surfaces of the metals to be coated in order to ensure proper mechanical adhesion of the coating to the given substrate. Preparation of the surface consisted in:

- chemical degreasing at 40–60 °C for 20 min,
- pickling in a solution of hydrochloric acid (steel) or sulphuric acid (copper) at ambient temperature for 10 min,

**Table 1 – Chemical composition, melting point and form of applied zinc-based solders [9].**

| Solder | Chemical composition, wt % | | Melting point, °C | Form/size, mm |
|---|---|---|---|---|
| | Zn | Al | | |
| L-ZnAl2 | 98 | 2 | 382–407 | Wire, dia. 1.6 |
| L-ZnAl4 | 96 | 4 | 382–387 | Wire, dia. 1.6 |
| L-ZnAl15 | 85 | 15 | 382–450 | Wire, dia. 1.0 |

**Table 2 – Chemical composition of aluminium AW-1050A.**

| Designation | | Chemical composition, wt% | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| PN | EN | Al min. | Fe Max. | Si Max. | Zn Max. | Ti Max. | Mg Max. | Mn Max. | Cu Max. | Ni Max. | Other Max. |
| A1 | AW-1050A | 99.5 | 0.40 | 0.25 | 0.07 | 0.05 | 0.05 | 0.05 | 0.05 | 0.05 | 0.03 |

**Table 3 – Chemical composition of materials used for soldered joints with aluminium.**

| Copper grade Cu-ETP acc. to EN 13601:2002<br>Chemical composition, wt% | | | |
|---|---|---|---|
| Cu | Bi, max. | Pb, max. | Other, max. |
| 99.90 | 0.001 | 0.005 | 0.004 |
| **Unalloyed steel grade DC01 acc. to EN 10130:2009<br>Chemical composition, wt% (rem. Fe)** | | | |
| C | Mn | P | S |
| 0.12 | 0.60 | 0.045 | 0.045 |

- anodic/cathodic degreasing at 40–60 °C for 6 min.

Surface roughness (Ra) of metals after the process was 0.18 μm for copper Cu-ETP and 0.99 μm for unalloyed steel DC01.

The coating Zn–Ni was applied in alkaline bath Enviralloy Ni 12-15, in that nickel content ranges from 12 to 15 wt%. In a 1000-ml glass beaker, filled with the Enviralloy bath, immersed was anode in form of a disc of nickel sheet and the material to be coated, constituting cathode. Ratio of surface areas of anode and cathode was 2:1. To ensure uniform replacement of electrolyte, it was necessary to apply continuous stirring of the bath with a magnetic stirrer rotating at 4 rpm.

After the Zn–Ni coating is applied, it had to be activated by brightening in 1–2% solution of HCl and next passivated in chromate bath TriPass ELV 3100 to make it bluish and ensure its high corrosion resistance, ten times higher than that of Zn coatings.

Parameters of the bath Enviralloy Ni 12-15 working in rack arrangement are given in Table 4 [15]. Maximum deposition speed of the Zn–Ni coating was 0.18 μm/min for bath temperature of 28 °C and cathode current density 2 A/dm$^2$ and its recommended thickness was from 12 to 16 μm. Zn–Ni coatings applied for soldering tests were 16 μm thick.

After applying the Zn–Ni layer on copper and steel substrates, its thickness was measured using an instrument Fischerscope type X-RAY XDL-B. The instrument is designed for thickness measurements and analysis of coatings by X-ray fluorescence. It permits measurements of very complicated systems of coatings without calibration standards with predictable measuring accuracy (±1 μm). During measurement, an X-ray beam bombards the coating. High radiation energy facilitates penetration and causes fluorescence of both coating and substrate. Thickness of a coating is determined by measuring X-ray fluorescence of the coating material: the more intensive fluorescence, the biggest thickness [16]. Average thickness of the applied layers was 15.93 μm on copper substrate and 15.98 μm on steel substrate.

## 4. Measurements of wettability and spreadability of zinc-based solders on Zn–Ni coating

In order to determine usability of the Zn–Ni layer for soldering processes performed were tests of wettability and spreadability of zinc-based solders on this layer. The tests were carried-out on Plates 50 mm × 50 mm and 0.5 mm thick (+ thickness of the applied layer). Solder wire was cut to sections ca. 1 mm long with mass of ca. 0.1 g, which were next covered with flux with mass equal to half mass of solder. The samples were placed on a mesh coated with ceramics situated on a tripod and heated-up from below with propane-air flame of a Bunsen burner. Time of heating was ca. 5 s since the solder become melted [7,8].

Surface area of spreading the zinc-based solders was calculated using the optical programme Olympus DP-Soft for digital processing of pictures with a function of planimetry. Measurements of spreadability of Zn-based solders on surfaces of the examined metals with applied Zn–Ni layer 16 μm thick are given in Table 5. They are average values of five measurements. Fig. 1 shows comparison of spreadability of Zn-based solders on substrates with no coating and with a Zn–Ni layer. Just before testing, the substrates with no coating were cleaned by manual grinding with abrasive paper No. 400 and degreased with Nitro solvent.

When analysing the examination results, attention should be paid to significant improvement of spreadability of Zn-based solders on copper surface with applied Zn–Ni layer in comparison with copper substrate without any layer. A

**Table 4 – Working parameters of Enviralloy Ni 12-15 bath in rack arrangement [15].**

| Parameter | Range | Optimum |
|---|---|---|
| Zinc concentration | 6–8 g/dm$^3$ | 7 g/dm$^3$ |
| Nickel concentration | 0.7–1.3 g/dm$^3$ | 1.1 g/dm$^3$ |
| Sodium hydroxide concentration | 110–120 g/dm$^3$ | 115 g/dm$^3$ |
| Sodium carbonate concentration | <80 g/dm$^3$ | |
| Temperature | 20–28 °C | |
| Cathode current density | 1.5–2.5 A/dm$^2$ | |
| Anode current density | 1.0–2.0 A/dm$^2$ | |

**Table 5 – Measurements of spreadability of zinc-based solders on surfaces of the examined metals with applied Zn–Ni coating.**

| Solder | Coating | Solder spreading area, mm$^2$ | |
|---|---|---|---|
| | | Copper Cu-ETP | Unalloyed steel DC01 |
| L-ZnAl2 | Zn–Ni | 268 | 276 |
| L-ZnAl4 | | 181 | 185 |
| L-ZnAl15 | | 119 | 127 |

characteristic feature of this coating is decrease of spreadability areas along with increasing aluminium content in the solders. This situation is opposite to that in the case of spreadability of Zn-based solders on copper surface with no coating [9]. There, spreadability on each material increased along with increasing aluminium content in the solders.

Measurements of wetting angles were taken on cross-sections in the middle of drops of spreaded solders and their results are given in Table 6. Fig. 2 shows comparison of wettability of substrates with applied Zn–Ni layer with wettability of substrates with no coating. These are average values of five measurements.

**Table 6 – Wettability of substrates with applied Zn–Ni layer with zinc-based solders.**

| Item | Solder | Coating | Wettability angle $\theta$,° | |
|---|---|---|---|---|
| | | | Copper Cu-ETP | Unalloyed steel DC01 |
| 1 | L-ZnAl2 | Zn–Ni | 4 | 5 |
| 2 | L-ZnAl4 | | 6 | 7 |
| 3 | L-ZnAl15 | | 7 | 8 |

The obtained results are satisfactory that is evidenced by small wetting angles whose average value, irrespective of kind of used Zn-based solder, does not exceed 10°. A special attention deserves significant improvement of copper substrate, as proved by many times smaller wetting angles. In the

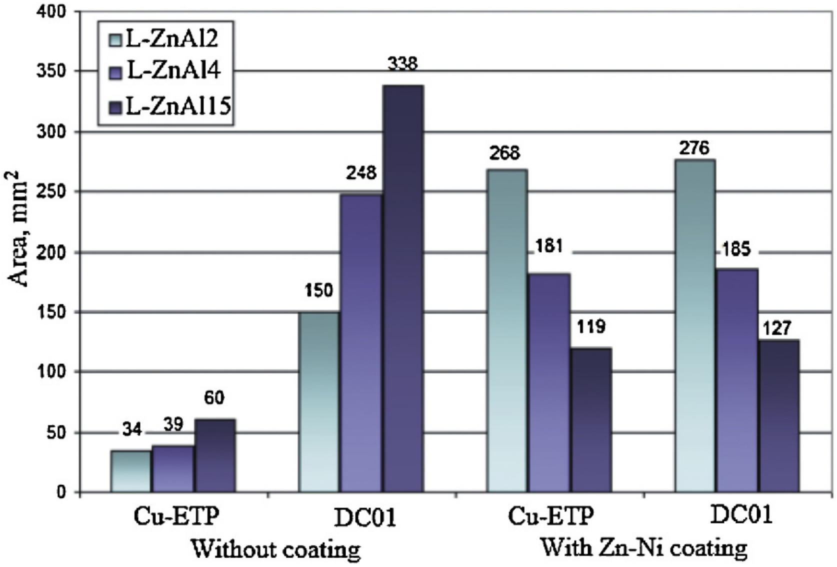

Fig. 1 – Spreadability of zinc-based solders on surfaces of the examined metals without and with applied Zn–Ni coating.

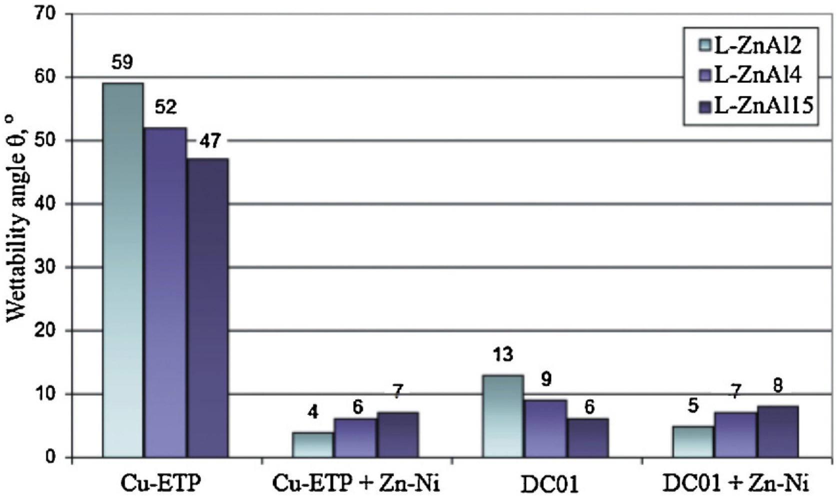

Fig. 2 – Wettability of copper and steel with and without applied Zn–Ni layer [5].

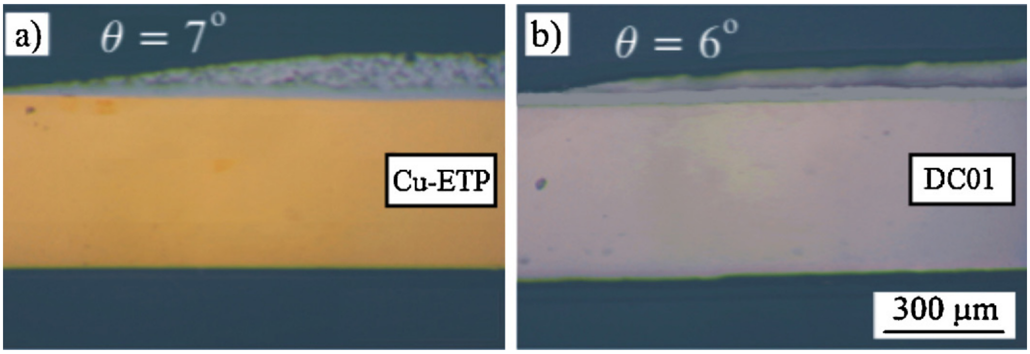

**Fig. 3 – Wettability of copper (a) and unalloyed steel (b) with applied 16 µm thick Zn–Ni layer by solder L-ZnAl4.**

case of copper substrate without Zn–Ni layer, this angle ranged between 47 and 59° depending on Al Content in Zn-based solders [8]. Fig. 3 shows exemplary wettability of steel and copper surfaces with applied Zn–Ni layer.

## 5. Metallographic examinations and microhardness measurements

For microscopic examinations prepared were overlap joints of aluminium AW-1050A with copper Cu-ETP and steel DC01, with 16 µm thick Zn–Ni layer applied on their surfaces. Joints were made with the solder L-ZnAl4. Their cross-sections are shown in Fig. 4. Width of soldering gap was 0.2 mm and was fixed by means of steel distance wires. The obtained joints are characterised by good filling of the gap on entire length of the joint.

Vickers microhardness was measured on cross-sections shown in Fig. 5, at the penetrator load 25 G, acc. to EN ISO 6507-1: 2007 [14]. On this ground, determined was influence of the applied Zn–Ni layer on hardness of the transition zone between remelted solder and copper or steel base metal, see Fig. 6.

As announced in [9], a relatively hard reactive zone is created at the interface between Zn-based solder and copper or steel, 7–15 µm or 12–21 µm wide, respectively. Hardness of the reactive zone ranges from 471 to 536 HV0.025 in the case of copper and from 317 to 522 HV0.025 in the case of steel. The reactive zone can be composed of intermetallic phases from the system Al–Cu and Al–Fe [12–14].

**Fig. 4 – Soldered overlap joints: Al–Cu-ETP + Zn–Ni layer (a) and Al–DC01 + Zn–Ni layer (b) made with L-ZnAl4 solder.**

As was assumed, the Zn–Ni layer applied on surfaces of copper and steel restricts creation of intermetallic phases on the interface between the solder joint and the substrate. This is proved by nearly three times lower hardness in the zone at the

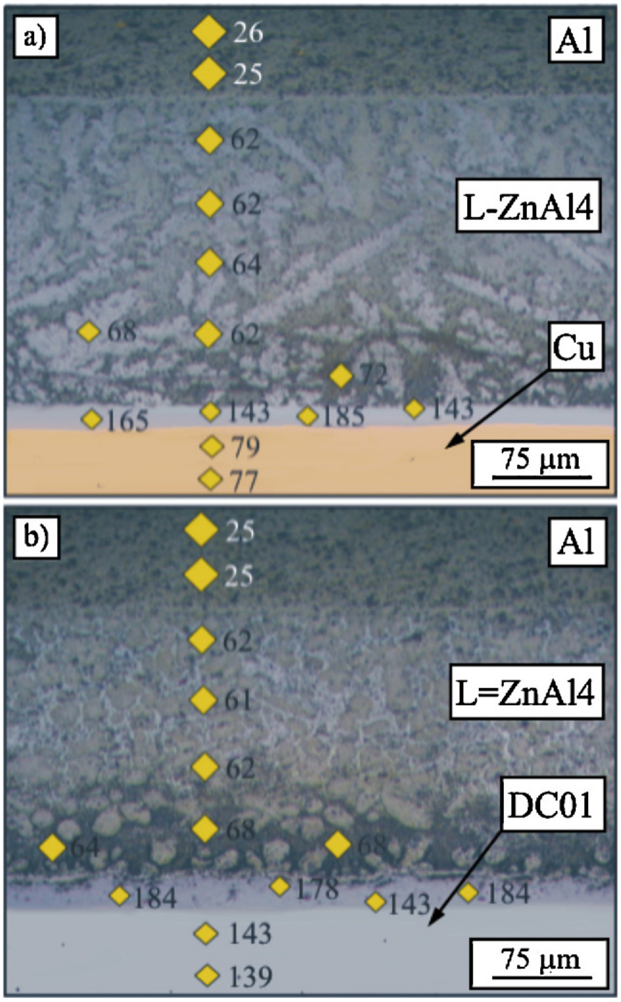

**Fig. 5 – Microhardness HV0.025 in soldered joints Al–Cu + Zn–Ni layer (a) and Al–DC01 + Zn–Ni layer (b), made with L-ZnAl4 solder [5].**

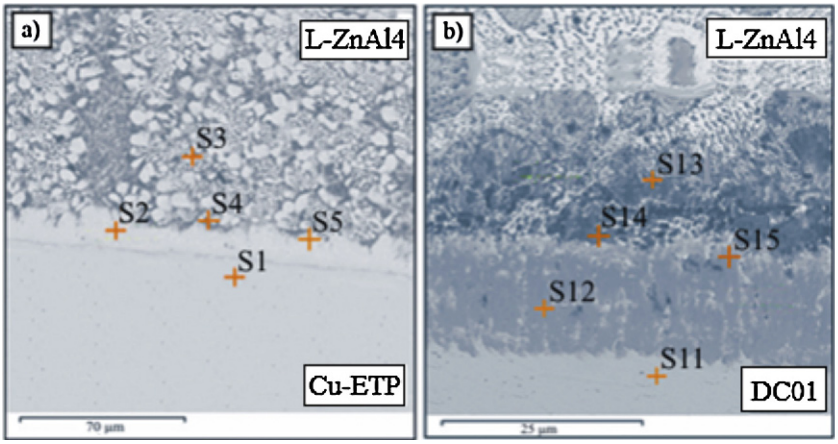

**Fig. 6 – SEM image of soldered joints Al–L-ZnAl4–Cu-ETP + Zn–Ni layer (a) and Al–L-ZnAl4–DC01 + Zn–Ni layer (b) with marked points of EDS analysis.**

interface in comparison to that in the joints without the intermediate Zn–Ni layer. This 16 µm thick layer reduces hardness of the reactive zone from over 500 HV0.025 to less than 200 HV0.025, which does not present any risk for functionality of soldered joints [5]. On the other hand, the joint can be of diffusive nature, which is proved by the dark zone ca. 50 µm thick, present directly above the galvanic Zn–Ni layer. Occurrence of diffusive phenomena results from relatively high soldering temperature, close to 450 °C.

In order to check, whether no intermetallic phases are created at the interface between solder and copper base, local EDS analysis was performed. The EDS analysis was carried-out using a scanning electron microscope TM3000 Tabletop Hitachi and an X-ray analyser SwiftED 3000 Oxford Instruments. Local EDS analysis was carried-out in five points of the joints Al–Cu-ETP + Zn–Ni layer and Al–DC01 + Zn–Ni layer, see Fig. 6a and b. Chemical analysis was performed also on the side of base material at ca. 5–10 µm from the applied galvanic coating. Chemical compositions in individual measuring points are given in Table 7.

As results from distribution of elements, the soldered joint Al–Cu includes in its galvanic Zn–Ni layer (point S2) mainly components of the Zn–Ni layer, with slight content of the components coming from the soldered material and the joint. Aluminium from the solder does not penetrate in large amounts to the Zn–Ni layer (0.71 wt% Al at S5), either. The copper substrate does not react with the Zn–Ni layer (point S1).

Traces of nickel (0.18 wt%) are found in the soldered joint directly above the Zn–Ni layer (point S4), which can prove that no intermetallic compounds containing Ni are present there. At 30 µm from the Zn–Ni layer (point S3), components of the soldered joint, i.e. Zn and Al, are exclusively present.

Like in the joints Al–Cu + Zn–Ni, the applied Zn–Ni layer in the joints type Al–DC01 (point S12) consists mainly of components of the Zn–Ni coating. At the interface between the soldered joint and the Zn–Ni layer, a small quantity of Ni is present at S14 (0.64 wt%) and a small quantity of Al is present at S15 (0.74 wt%). On the side of the base material (DC01 steel), no presence of the elements composing the Zn–Ni layer was found, which proves absence of its reaction with the substrate.

## 6. Static shear test of dissimilar-metal soldered joints

Static shear test of dissimilar-metal soldered joints was carried-out on overlap joints made by heating with propane-air flame. Time of soldering ranged between 49 and 56 s.

**Table 7 – Results of EDS analysis in the joints Al–L-ZnAl4–Cu-ETP + Zn–Ni layer and Al–L-ZnAl4–DC01 + Zn–Ni layer.**

| Test point | Chemical composition, wt% | | | | | |
|---|---|---|---|---|---|---|
| | Fe | Cu | Zn | Al | Ni | Other |
| S1 | – | 99.90 | – | – | – | 0.1 (Bi, Pb) |
| S2 | – | 0.19 | 86.13 | 0.31 | 13.37 | – |
| S3 | – | – | 93.28 | 6.72 | – | – |
| S4 | – | – | 92.97 | 6.85 | 0.18 | – |
| S5 | – | – | 86.03 | 0.71 | 13.26 | – |
| S11 | 99.19 | – | – | – | – | 0.81 (C, Mn, P, S) |
| S12 | – | – | 85.69 | 0.59 | 13.72 | – |
| S13 | – | – | 94.13 | 5.87 | – | – |
| S14 | – | – | 93.18 | 6.18 | 0.64 | – |
| S15 | – | – | 85.28 | 0.74 | 13.98 | – |

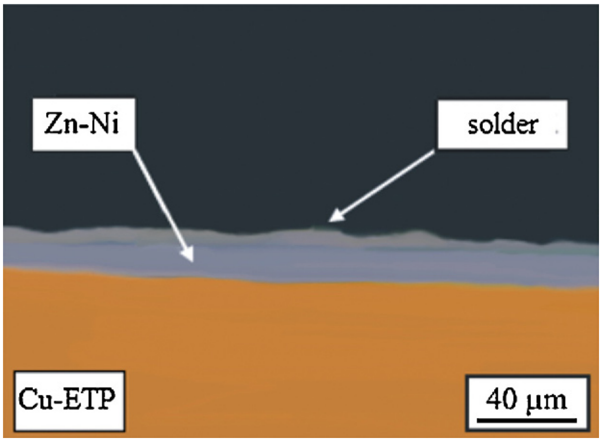

**Fig. 7 – Cross-section of copper test piece with applied Zn–Ni layer after static shear test.**

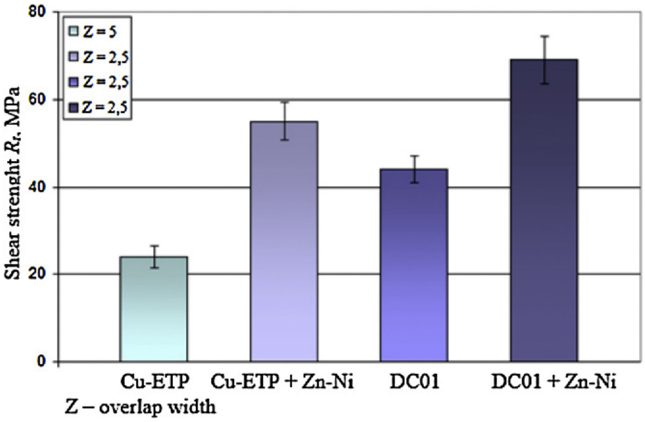

**Fig. 9 – Comparison of shear strength soldered joints Al–L-ZnAl4–Cu-ETP and Al–L-ZnAl4–DC01 without and with applied Zn–Ni layer.**

Prepared were two kinds of dissimilar-metal soldered joints: Al–Cu + Zn–Ni layer and Al–DC01 + Zn–Ni layer. The joints were made with the L-ZnAl4 solder, because of small influence of aluminium content in Zn–Al alloy on strength of joints [9]. Static shear test was performed on a testing machine Instron model 3369, using a grip with distance inserts. Crosshead speed was 0.2 cm/min and load range was up to 50 kN.

Overlaps in the joints Al–Cu was 5.0 mm wide, both with and without the Zn–Ni layer. The test piece with the joint containing the Zn–Ni layer was fractured in heat-affected zone in aluminium, at 73.0–76.0 MPa. An attempt was made to reduce width of the overlap from 5.0 mm to 2.5 mm. In this case, the joint was fractured on the side of copper. Average value of shear strength was 54.5 MPa, over twice higher than in the case of the joints Al–Cu without the Zn–Ni layer and with the overlap 5.0 mm wide (24.6 MPa) [9].

Fig. 7 shows cross-section of a test piece after static shear test, evidencing cohesive fracture within the soldered joint, beyond the Zn–Ni layer. Cohesive nature of the fracture proves also good adherence of the Zn–Ni layer to the copper substrate.

The joints Al–DC01 + Zn–Ni layer were made with the same overlap width (2.5 mm) [9] as in the joints without any applied Zn–Ni layer. In three of five cases, fractures occurred in heat-affected zones in aluminium, under stress values within 74.0–76.5 MPa. In two cases, the test pieces were broken by decohesion of soldered joints under stress values of 65.3 MPa and 64.9 MPa, respectively (Fig. 8). This proves good adherence of the Zn–Ni layer to the steel substrate.

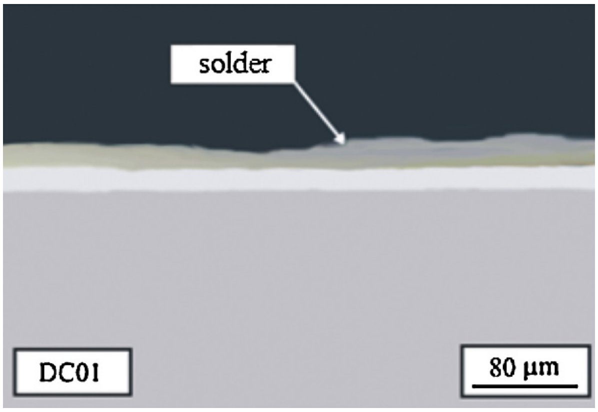

**Fig. 8 – Cross-section of steel test piece with applied Zn–Ni layer after static shear test.**

Comparison of shear strength of soldered joints Al–L-ZnAl4–Cu-ETP and Al–L-ZnAl4–DC01 without and with applied Zn–Ni layer 16 μm thick is shown in Fig. 9.

## 7. Conclusions

On the grounds of the carried-out examinations, the following conclusions can be formulated:

- A Zn–Ni layer 16 μm thick, applied on surface of copper Cu-ETP, results in significant improvement of wettability and spreadability of zinc-based solders on copper surface.
- A Zn–Ni layer 16 μm thick, applied on surfaces of copper Cu-ETP and unalloyed steel DC01, effectively restricts creation of intermetallic phases on the interface between base metal and zinc-based solders, with no occurrence of a hard reactive zone.
- Application of a Zn–Ni layer on surface of copper Cu-ETP results in over double increase of shear strength of soldered joints with aluminium.
- A Zn–Ni layer 16 μm thick, applied on surface of unalloyed steel DC01, results in increase of mechanical strength of soldered joints and final fracture of a joint happens in base material (Al) in heat-affected zone or by decohesion within the soldered joint.

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